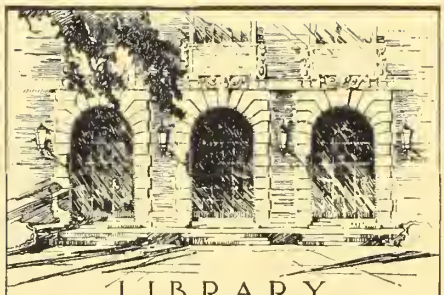


TABLE OF CONTENTS
INORGANIC SEMINAR ABSTRACTS

TABLE OF CONTENTS
1965-1966

Table of Contents (continued)

BONDING AND STRUCTURE IN PLATINUM-OLEFIN COMPLEXES

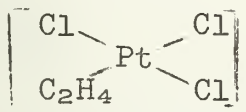
Marlene Kresge September 28, 1965

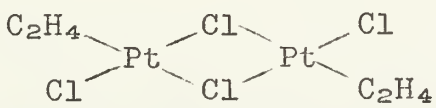
In 1827, Zeise (1), upon reacting platinic chloride and ethanol, obtained the compound today recognized as Zeise's acid, $H[Pt(C_2H_4)Cl_3]$. In the ensuing years much has been published on the preparations, general properties, and reactions of these and related Pt(II)-olefin complexes. The reviews by Keller (2) and Chatt (3) are recommended for a thorough treatment of this material.

Progress in the development of a theory of bonding which satisfactorily fit all the data was not made until the 1950's. Crystal structure data was nonexistent. Since then, infrared, n.m.r., and X-ray data, in conjunction with the wealth of chemical data already available, have provided the basis for a theoretical understanding of these complexes.

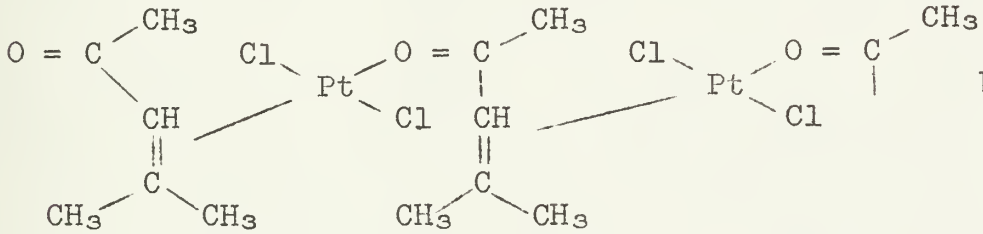
TYPES OF KNOWN COMPLEXES

Monoolefins



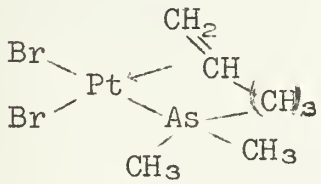


nonbridging



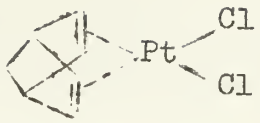
bridging (4)

$Pt(C_3H_6)(C_2H_4)Cl_2$ mixed (5,6)

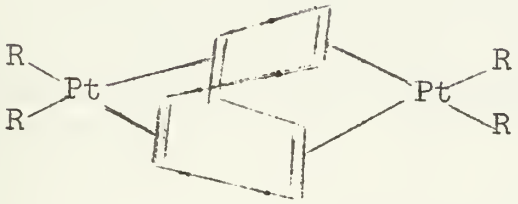


terminal chelate (7)

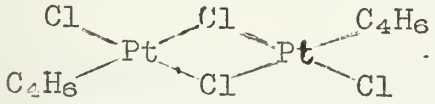
Diolefins



terminal chelate (8)



bridging chelate (9)



terminal (10)

BONDING

In 1951, Chatt (11), upon finding all existing theories unacceptable, proposed his ethylidene structure for Zeise's ion. At the same time, J. S. Dewar (12) proposed a new bonding scheme for silver-olefin complexes. He suggested that the bond consisted of two parts--a σ bond caused by the overlap of an empty silver s orbital with a filled olefinic π orbital and a π type bond created by overlap between a filled d orbital on silver and an empty olefinic antibonding orbital. Chatt, realizing that not only did his model involve the migration of one of the olefinic protons, but that the structure did not agree with the infrared spectra obtained, turned to an appropriate modification of Dewar's structure (13). Like Dewar's proposal, the bonding consisted of two parts. In Chatt's model, however, the σ bond results from overlap of a Pt dsp^2 hybrid with a filled olefinic π orbital and for best overlap, the "back-bond" involves a filled Pt dp hybrid and an empty olefinic π antibonding orbital. This then led, as shown in figure 1, to a configuration with the double bond perpendicular to the $[PtCl_3]^-$ plane.

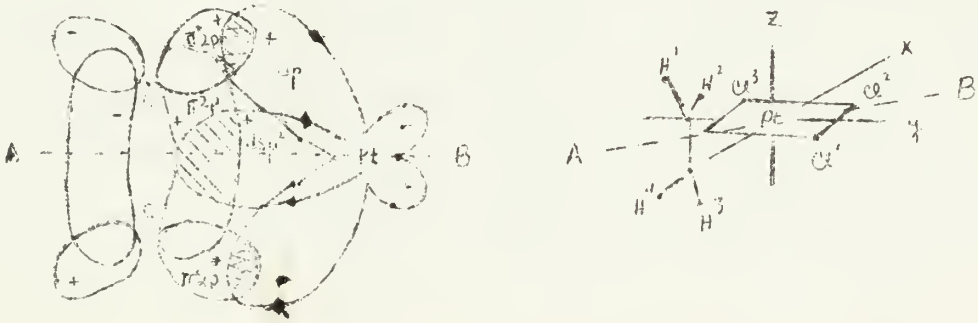


Fig. 1 (13)

Since this bonding scheme was quite successful in explaining the data then known, it gained wide acceptance. In Russia, however, Gel'man(14) maintained that bonding was through a three-member ring similar to that in cyclopropane and ethylene disulfide. It was not until 1960 that this view was finally dispelled (15, 16) by n.m.r. and I.R. data.

Normally, free olefins, if they are infra-red active, exhibit a C=C stretching frequency in the neighborhood of 1650 cm^{-1} and a =CH bending mode above 3000 cm^{-1}. On complexation, it was found that the bands above 3000 cm^{-1} remained and were shifted to somewhat higher frequencies, while the C=C stretch was shifted 70 - 200 cm^{-1} lower (see table 1).

Table 1

Complex	ν C=C cm^{-1} of free olefin	ν C=C cm^{-1} of complex	lowering cm^{-1}	Ref.
$K[Pt(C_2H_4)Cl_3]$	-	1527(KBr)	-	13 17,18
" "	-	1516(Nujol)	-	17
$[(C_2H_4)PtCl_2]_2$	-	1511(KBr)	-	17
" "	-	1506(Nujol)	-	13
<u>trans</u>-$[Pt(C_2H_4)(NH_3)Cl_2]$	-	1520	-	18
$[Pt(C_4H_8)Cl_2]Cl_2$	1648	1501	147	17
$[Pt(C_{10}H_{16})Cl_2]$	1647	1512	135	19
$[Pt_2(C_{10}H_{16}OCH_3)_2Cl_2$	1647	1505	142	19
$PtCl_3(allyl_2NH_2)$	1650	1500	150	20
$Pt\{As(CH_3)_2(CH_2)_3CHCH_2\}Cl_2$	1637	1505	132	7
$[Pt(C_3H_6)Cl_3]^-$	1647	1504	143	13

In ethylene complexes, the presence of a band attributed to a lowered olefinic C=C stretch immediately signified a loss of symmetry, and coordination through the double bond. Since the uncoordinated and coordinated spectra varied only in the C=C frequency, and since these shifted peaks were of low intensity, it was held that the C=C bond might be considered a perturbed double bond.

Using the lowered frequencies found for $[Pt(C_2H_4)Cl_2]_2$, $K[Pt(C_2H_4)Cl_3]$, $(Pt(i\text{-butene})_2Cl_2)_2$, $[Pt(i\text{-butene})Cl_2]_2$, and $[Pt(butene\text{-}1)Cl_2]_2$, Jonassen and Field (17) calculated force constants for the carbon-carbon link. They obtained a value k = 8.03. Since values of k = 9.6 are common for a double bond compared to 4.9 for a single bond, they concluded that the multiple bond in the coordinated olefin has an order of one and two-thirds.

Further support for a perturbed double bond was given by Oppegard (21), who found that the IR spectra of <u>cis</u>- and <u>trans</u>-2-pentene Pt(II) complexes were different. It was therefore suggested that the carbon-carbon link was rigid and that no isomerization was possible. This was later confirmed (22) when decomposition of 1,3-bis-(<u>cis</u>-2-butene)-2,4-dichloro-μ-dichloroplatinum(II), $(C_4H_8PtCl_2)_2$, gave back the original <u>cis</u>-2-butene, and likewise, the <u>trans</u> olefinic complex yielded the <u>trans</u> olefin.

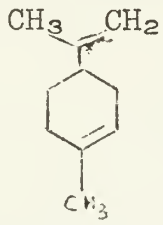
Considering the olefinic molecule as a whole, recent investigations have shown that it is distorted only to a slight degree, if at all. Maričić (23) found by single crystal n.m.r. work that in $K[Pt(C_2H_4)Cl_3]\cdot D_2O$ there is little difference in the olefin interproton distance compared with that found in the free olefin. Reeves (24) pointed out that the ethylene molecule in $[Pt(C_2H_4)Cl_2]_2$ has an interproton distance intermediate between that of C_2H_4 and an ethane molecule with two protons removed. This single crystal work has also shown that no molecular rotation occurs in these compounds. However, it was found that in Zeise's salt there are "large-amplitude rotational oscillations" about both the C=C bond axis and an axis perpendicular to the C_2H_4 molecular plane (24).

CHELATION

For many years it was thought that only one olefinic molecule could be accommodated per Pt(II) atom, and that, regardless of the number of double bonds it contained, the olefin would only complex through one of them. In 1952, however, Chatt and Wilkins (5, 25) prepared the unstable <u>trans</u>-$[Pt(C_2H_4)_2Cl_2]$, thereby disproving the first claim. Soon many diolefins as well as many monoolefins which contain a second donor site were found to chelate (see table 2).

Table 2

Chelating Diolefins:



Dipentene (DP)
$C_{10}H_{16}$
(19)

Dicyclopentadiene (DCP)
$C_{10}H_{12}$ (18)

1,3,5,7-cyclo-
octatetraene
(COTT) C_8H_8

(9)

Cyclooctа-1,5-diene
(COD) C_8H_{12}
(19, 26)

Norbornadiene (NBD)
C_7H_8 (27)

Cycloheptatriene (CHT)
1,5-hexadiene (HEX)
Diallyl Ether (DAE) (28)

Chelating Monoolefins:

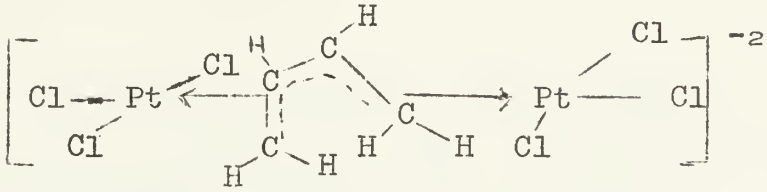
$As(CH_3)_2(CH_2)_3CH = CH_2$ (7)

$(CH_2 = CHCH_2)_2NH$ (29)

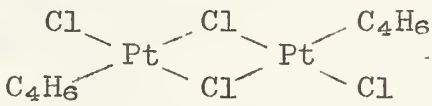
Allylamines (20)

Butadiene, however, would not chelate, but instead was found to coordinate in one of two ways:

1) as a single allylic bridge (30, 31)



2) as a monoölefin (10)



The inability of butadiene to chelate led Doyle and Jonassen (32) to state that "the ability of certain olefins to chelate with Pt seems to depend on the distance between the double bonds and the ability of the molecule to assume a configuration in which the axes of the double bonds are in the same plane and approximately parallel to each other". The second of these is not without exception. Since the double bond must be normal to the plane of the molecule for best overlap, the most stable complexes are formed under such conditions. However, as was shown in the crystal study of dipentene Pt(II) chloride (33), the two double bonds need not be so oriented. As is to be expected, with the loss of this parallelism, stability is also lost.

The first of Doyle and Jonassen's statements, however, has been well substantiated. Adding 1,5-hexadiene to an aqueous solution of K_2PtCl_4, Jensen (34) obtained $PtCl_2 \cdot C_6H_{10}$ and also the analogous iodide complex. With the 2,4-hexadiene, however, reaction with the chloride gave metallic platinum and the iodide gave black PtI_2. Also, diallyl ether yielded a chelate, $[Pt(C_6H_{10}O)Cl_2]$, but divinyl ether $[(CH_2 = CH)_2O]$ gave only metallic platinum. That the complexes obtained were indeed chelated was further shown by large dipole moments (6-7D in benzene) and by cryoscopic measurements which indicated their monomeric nature. It would seem then that linear conjugated systems will not chelate.

Cycloöctatetraene, COTT, has been included in the list of chelating diolefins since only two of its double bonds (those which are nonadjacent) will coordinate to a given Pt (35). By reaction of the iodide (Fig. 2)

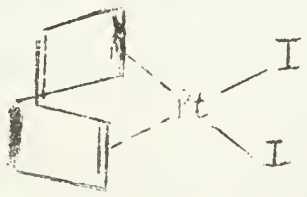
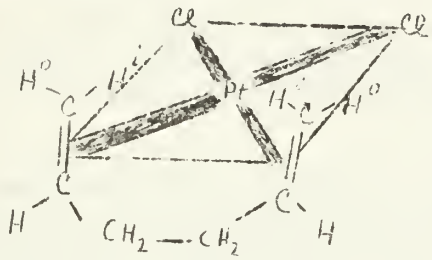


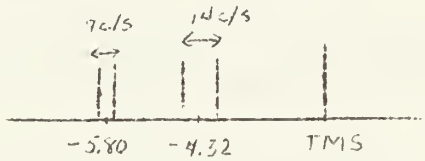
Fig. 2 (34)

Fig. 3 (9)

with a Grignard reagent, $RMgI$, a dimer (36) is obtained which has been assigned the bridging structure (9) shown in Fig. 3. The COTT is depicted as having D_{2d} symmetry solely on the basis of Karle's (37) electron diffraction studies on the free ligand. No information concerning its conformation once complexed could be obtained.

Cramer (38, 39) has shown that unsymmetrical olefinic protons can be detected in the chelated complexes even though the rate of olefinic exchange is quite rapid for Pt(II) complexes. The rate exhibited by the chelates is much slower than that of the monoolefinic complexes. Therefore, he was able to obtain the following spectrum for 1,5-hexadienedichloroplatinum(II):





CRYSTAL STRUCTURES

To date not much X-ray work has been done on the olefin-Pt(II) complexes. Table 3 lists the data currently available.

Table 3

Compound	Space Group	Molecules per unit cell	Crystal Class	Ref.
$K[Pt(C_2H_4)Br_3]\cdot H_2O$	$P2_1$	2	-	40
$K[Pt(C_2H_4)Cl_3]\cdot H_2O$	$P2_1$	2	monoclinic	41 42
$Pt(C_2H_4)\ NH_3Br_2$	C_{4h}^6	16	tetragonal twinning	43
trans-$[Pt(C_2H_4)\{NH(CH_3)_2\}Cl_2]$	$P2_1/n$	2	monoclinic	44
$Pt(C_{10}H_{16})Cl_2$	$P2_1cn$	4	orthorhombic	32
$(R_2Pt)_2C_8H_8$	$C2/c$	4	monoclinic	35
cis-$[Pt(NH_3)(C_2H_4)Cl_2]_2$	$D_{4h}^{19}=I4/amd$	16	-	45 46

The normal Pt-N and Pt-Cl bond distances are assumed to be 2.06 (s.d. 0.025 Å) and 2.34 (s.d.0.005Å) respectively (47). In the crystal studies done on $K[Pt(C_2H_4)Cl_3]$ (41, 42) and cis-$[Pt(C_2H_4)NH_3Br_2]$ (40), it was found that the Pt-halogen bond trans to the olefin was somewhat lengthened (2.42 and 2.51). For the trans-ethylene dimethyl amineplatinum(II) chloride (44), on the other hand, the trans Pt-N bond was found to be of the normal length (2.02A). Alderman et al. (44) have developed a theory which explains this seemingly inconsistent data. They maintain that the high trans effect of the olefin modifies the π molecular bonding system only. This modification will lengthen any trans ligand-Pt bond containing double bond character, while any trans bond devoid of such character will not be affected.

In all the analyses, the C=C bond was found to be longer than the normal 1.34A, falling within the range 1.47-1.56Å. This then further confirms the n.m.r. and IR findings of a slightly perturbed double bond.

In most cases the double bond was perpendicular to the plane of the molecule, as was expected from previous work on Pd-olefin complexes. In the dipentene Pt(II) chloride crystal, however, it was observed (33) that both double bonds were not so oriented (see fig. 4)

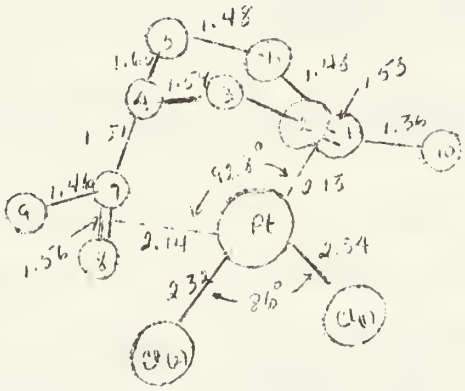


Fig. 4 (33)

Here $C_{(1)}=C_{(2)}$ is indeed perpendicular as expected, but $C_{(7)}=C_{(8)}$ makes an angle of 62° with the intersection of the Pt-$Cl_{(1)}$-$Cl_{(2)}$ and $C_{(4)}$-$C_{(7)}$-$C_{(8)}$-$C_{(9)}$ planes. This inclination lessens the overlap of the Pt dp hybrid and the π antibonding orbital on the olefin. No back-bonding can occur, therefore, between $C_{(7)}=C_{(8)}$ and Pt. It is proposed that this bond weakening results in the relative instability of the dipentene complexes with respect to other chelated diolefins complexes as noted by Chatt (19).

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SOME CHEMISTRY OF THE $B_{10}H_{10}^{2-}$ AND $B_{12}H_{12}^{2-}$ IONS

Harlan L. Lewis October 5, 1965

INTRODUCTION

The synthesis and characterization of these two polyhedral boron hydride anions has opened a highly unusual and interesting area in boron hydride chemistry, quite unlike that of the neutral boron hydrides.

STRUCTURAL INFORMATION

1. From X-Ray Work:

Lipscomb and co-workers (1,2) have determined the structure of $B_{10}H_{10}^{2-}$ from $Cu_2B_{10}H_{10}$. Its space group is Pcab and there are eight molecules per unit cell. The tetragonal pyramid geometry resembles that of B_5H_9, and the boron-boron distances were given as: apex-edge 1.73 A, edge-edge 1,86 A, and cross equatorial 1.82 A. Description of the Cu(I)-B bonding was also given.

Wunderlich and Lipscomb (3) placed the $B_{12}H_{12}^{2-}$ ion in space group T_h^3-$Fm3$ (from $K_2B_{12}H_{12}$) with four molecules per unit cell. Crystal boron-boron distances were ± 0.01 A from the idealized icosahedral distance of 1.77 A (mean).

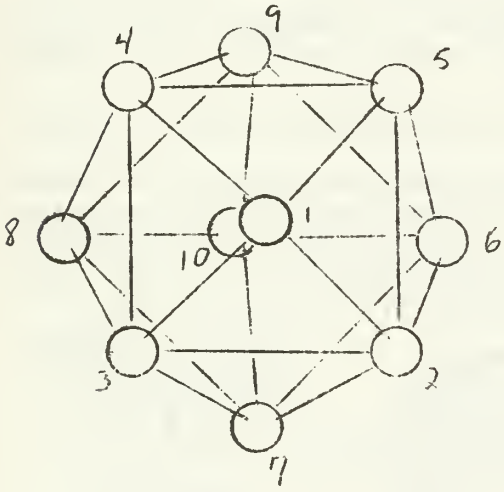

Fig. 1 (29)

$B_{10}H_{10}^{2-}$

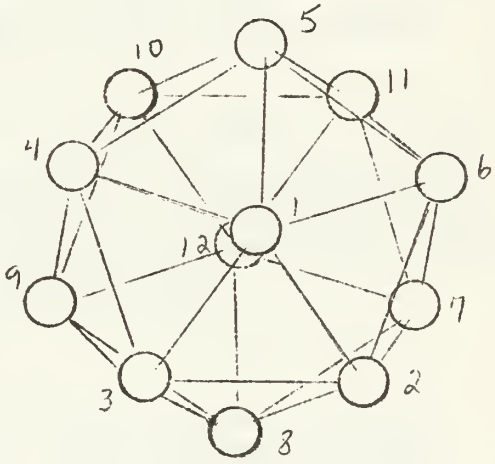

Fig. 2 (29)

$B_{12}H_{12}^{2-}$

2. From Infrared and Raman Spectra:

The D_4d structure for $B_{10}H_{10}^{2-}$ should give rise to twelve infrared fundamentals, six polarized and thirteen depolarized Raman lines. Some assignments have been made (4,5), but analysis is incomplete.

On the other hand, the I_h symmetry of $B_{12}H_{12}^{2-}$ has yielded complete assignment of the three infrared fundamentals, two polarized and four depolarized Raman lines (4,5), as predicted.

Neither anion has absorption maxima in the visible or u.v. down to 200 mμ where strong end absorption occurs.

3. From NMR Spectra:

The B^{11} spectrum of $B_{10}H_{10}^{2-}$ consists (5,6,7) of two doublets, intensity ratio 1:4, which collapse under double resonance (at 60 mc) to two singlets. The H^1 spectrum contains a broad "equatorial" quartet and a sharp "apical" quartet. Double resonance (at 19.2 mc) yields two singlets, intensity 1:4.

The B^{11} spectrum of $B_{12}H_{12}^{2-}$ (5,8) consists of a doublet which collapses to a singlet under 60 mc radiation, while the H^1 spectrum is a broad plateau bounded by two broad separate peaks, which collapse to a sharp singlet upon decoupling with 19.2 mc radiation.

PREPARATIONS

1. $B_{10}H_{10}^{2-}$

The first preparation of this ion occurred as a side reaction (9,10) during an addition reaction using Lewis bases with $(CH_3CN)_2B_{10}H_{12}$, as;

$$(CH_3C{\equiv}N)_2B_{10}H_{12} \xrightarrow{HY} \left(CH_3\underset{Y:}{C}{=}\overset{H}{N}\right)_2 B_{10}H_{12} \longleftrightarrow \left(CH_3\underset{Y}{C}{-}\overset{H}{\underset{\cdot\cdot}{N}}\right)_2 B_{10}H_{12} \qquad \text{(i)}$$

where HY was a primary or secondary amine. However, when tertiary amines such as triethyl amine were used (Y),

$$(CH_3C{\equiv}N)_2B_{10}H_{12} \xrightarrow{Y} Y_2B_{10}H_{12} + (B_{10}H_{10}^{2-})\ (HY^{+})_2 + CH_3CN \qquad \text{(ii)}$$

where the products resulted from a displacement of acetonitrile and one portion of product, ionic in nature, appeared to have lost "cage" hydrogens to the triethylamine. In subsequent work, Pitochelli, et. al. (11), postulated a boron-boron bonding rearrangement:

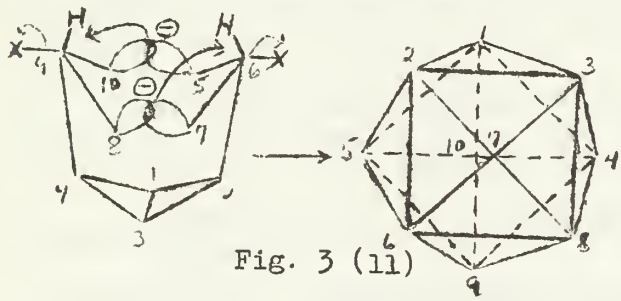

Fig. 3 (11)

The numbering scheme here conforms to that of $B_{10}H_{14}$ (11).

When these workers similarly converted 1,2,3,4,-$B_{10}H_{10}D_4$ to $B_{10}H_6D_4^{2-}$, comparison of its B^{11} n.m.r. with that of $B_{10}H_{10}^{2-}$ gave the following results:

		in ppm relative to $(CH_3O)_3B$	J_{B-H}
$(Et_3NH)_2B_{10}H_{10}$	axial	18.8 ± 0.5	138
$(Et_3NH)_2B_{10}H_{10}$	equatorial	47.0 ± 0.5	125
$(Et_3NH)_2B_{10}H_6D_4$	axial	19.0 ± 0.5	143
$(Et_3NH)_2B_{10}H_6D_4$	equatorial	48.1 ± 0.5	broad singlet

From this and the presence of deuterium exchange (B-H and N-H) for $B_{10}H_{10}[HN(C_2H_5)_3]_2$ in D_2O as opposed to no exchange for $B_{10}H_{12}[N(C_2H_5)_3]_2$ (10) the authors concluded the mechanism shown in Fig. 3 (11). [Confusingly, Pitochelli, et. al. (11) stated that $B_{10}H_{10}^{2-}$ did not undergo D exchange with D_2O or $(C_2H_5)_3ND^+$. However, Muetterties, et. al. (5) showed that this was primarily pH dependent.]

Heying and Naar-Colin also showed that (12)

$$(C_2H_5)_2S\text{-}2\text{-}BrB_{10}H_{11} + 2(C_2H_5)_3N \longrightarrow [(C_2H_5)_3NH]_2B_{10}H_9Br + 2(C_2H_5)_2S + H_2 \quad \text{(iii)}$$

where an equatorial B-Br bond remained intact, as also in

$$1\text{-}C_2H_5B_{10}H_{13} + 2(C_2H_5)_3N \longrightarrow [(C_2H_5)_3NH]_2B_{10}H_9C_2H_5 + H_2 \quad \text{(iv)}$$

Muetterties, et. al. (5), have also found a high yield preparation in

$$B_{10}H_{14} + 2(CH_3)_2S \xrightarrow{-H_2} B_{10}H_{12}\cdot 2(CH_3)_2S \xrightarrow[\text{liq.}]{NH_3} 2(CH_3)_2S + (NH_4)_2B_{10}H_{10} > 70\% \quad \text{(v)}$$

2. $B_{12}H_{12}^{2-}$

Pitochelli and Hawthorne first obtained a $B_{12}H_{12}^{2-}$ salt (8) in 3.8% yield from reaction of $2\text{-}B_{10}H_{13}I$ with triethylamine, while Heying and Naar-Colin (12) obtained, in a similar fashion with $2\text{-}B_{10}H_{13}Br$, and 8.6% yield.

Starting much more simply, first Muetterties group (13,14) and later, the Schaeffer group (15), were able to outline a general method for this anion. Thus Schaeffer used $B_3H_8^-$

$$NaB_3H_8 \xrightarrow[\text{diglyme 16 hrs.}]{\text{1. reflux in}} \text{2. } \xrightarrow{(CH_3)_3NHCl} \text{a } B_{12}H_{12}^{\ 2-} \text{ salt (65\%)} \quad \text{(vi)}$$

while Muetterties used a volatile low m.w. boron hydride with either a base-borane complex

$$2(C_2H_5)_3NBH_3 + 5B_2H_6 \xrightarrow[100\text{-}180^\circ]{} [(C_2H_5)_3NH]_2B_{12}H_{12} + 11\ H_2 \quad \text{(vii)}$$

or with a metal borohydride

$$2NaBH_4 + 5B_2H_6 \xrightarrow[100\text{-}180^\circ]{(C_2H_5)_3N} Na_2B_{12}H_{12} + 13H_2 \quad \text{(viii)}$$

A sequential buildup of polyhedral boranes was postulated (14) as occurring with a hydride ion or any borohydride, e.g. BH_4^-,

$B_3H_8^-$, etc. and a boron hydride interacting, most simply, in the following manner:

$$aH^- + bB_xH_y \longrightarrow [B_{bx}H_{by} + a - z]^{a-} + (z/2)\ H_2 \qquad \text{(ix)}$$

The authors (14) reported, however, that $B_{10}H_{10}{}^{2-}$ could not be prepared by this route in any appreciable yield (<1-2%), cf. (14).

Greenwood and Morris (16), using $B_{10}H_{14}$ and a base-borane complex, were able to obtain a 76% yield of $B_{12}H_{12}{}^{2-}$. These workers also found that by using $L_2B_{10}H_{12}$ in place of $B_{10}H_{14}$ and varying the ligand " L " gave either no reaction, $B_{10}H_{10}{}^{2-}$ or $B_{12}H_{12}{}^{2-}$ as the major product.

At about the same time as the work of Muetterties was reported, Adams, et. al. (17) reported a reaction similar to (viii) using a BH_4^- salt with $B_{10}H_{14}$.

VALENCE STRUCTURE AND REACTIVITY

1. Valence Theory

The molecular orbital descriptions of the two anions have been worked out by Lipscomb's group (6,18,19,20) and by Roberts and Longuet-Higgins (21). Since degeneracies arise in the one-electron approximations (20) to these two ions, energy gaps develop between levels which allow a more simple description of the " cage " structures than for similar "open" anions. In general, for n atomic orbitals (ϕ_i) and m valence electrons (m<n), bonding molecular orbitals are filled, while antibonding are not. Three-center boron bonding gives rise to one filled bonding orbital and two unfilled antibonding orbitals per three boron set. Presuming a normal two-center B-H bond, and using a three-center LCAO treatment on the "cages", Lipscomb's group (18,19) obtained the energies of the levels for a three-center treatment. In a more sophisticated treatment using physical factorizations of a 5N secular equation for the entire ions (20) Hoffmann and Lipscomb were able to determine the ordering of all levels in the polyhedral frameworks.

Then, as a check upon and correction to the LCAO-MO model, Hoffmann and Gouterman (22) described a crystal field model for the two anions. In this way the authors arrived at what they believed was a correct energy-level ordering for $B_{10}H_{10}{}^{2-}$ and $B_{12}H_{12}{}^{2-}$, and were also able to show that earlier assumptions that the coulomb integrals for the 2s and 2p atomic orbitals were equal, was invalid. Therefore an aromatic hydrocarbon analogy to these two ions for determining valence structures, as proposed by other investigators (see 22) was incorrect.

Subsequently, Hoffmann and Lipscomb (23) gave a population and charge distribution analysis for $B_{12}H_{12}{}^{2-}$. The results of all this work, and a summary paper by these authors (24) was as follows.

$B_{10}H_{10}{}^{2-}$ is a D_4d bicapped tetragonal antiprism. Its B^{11} n.m.r. spectrum was explained by assuming that the apical boron valence orbitals are slightly less symmetric than those of the equatorial borons (6), giving a slightly greater temperature

independent paramagnetism to the apical borons. The closed shell electron distribution based on the D_4d representation yields five filled bonding orbitals (A_1, E_1 and E_3) while the weakly bonding E_2 and nonbonding B_1 and B_2 are unfilled. Ten pairs of electrons go to the B-H bonds, and the remaining six pairs are distributed evenly to the framework B_5 groups (6).

$B_{12}H_{12}^{2-}$ is a D_5d bicapped pentagonal antiprism or icosahedron (I_h), (18, 21). There are twenty-five electron pairs in the closed shell structure; twelve pairs in the B-H bonds, the remaining thirteen pairs being in the "cage" bonding orbitals. There are thirty-six molecular orbitals in the polyhedron, and the filled levels are: one pair in Γ_{1g} (A_{1g}), three in Γ_{2u} (F_u), five in Γ_{5g}($E_g + F_g$), and the remaining four in Γ_{4u} ($A_u + F_u$), (18).

2. Substitution Predictions (Electrophilic)

Hoffmann and Lipscomb, using their charge distribution analyses (24) have predicted orders for sequential substitution on these two anions (25). They distinguish two separate cases for each anion.

For $B_{12}H_{12}^{2-}$, the first group may go anywhere. If this first group then exerts a positive (electron source) resonance or inductive effect then the second substituent would prefer: 2=3=4=5=6>7=8=9=10=11>12. The third group onto a 1,2-substituted $B_{12}H_{12}^{2-}$ would prefer position 3 or 6, etc. If the first group on is electron withdrawing, fifteen symmetry non-equivalent pathways exist for inductive withdrawal, and even more for resonance withdrawal.

For $B_{10}H_{10}^{2-}$, positions 1 and 10 are first. For a +R or +I effect, the third substituent may go anywhere, while the fourth group prefers 6 or 9, or less favorably 3 or 5. For a -R effect the order from the third substituent on is 2,8,3,9,4,7,5,6. For a -I effect of the first two groups, four alternate routes exist.

Haas (26) has also predicted the number of geometrical isomers for both anions, for $B_{10}H_{10-n}X_n$ (n = 1,2,...,5) and $B_{12}H_{12-n}X_n$ (n = 1,2,...,6). He also suggested that in halogenation at least, directive effects were overridden by random substitution based on collision rates.

REACTIONS

1. General Properties

These two anions, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, have been found to be quite unlike the molecular boron hydrides, for the former are stable to strong acids and bases, and are much less susceptible to oxidative degredation. Their chemistry is comparable to aromatic chemistry, for they readily undergo electrophilic substitution, and they are more reactive than benzene toward most electrophiles (27,28). They form thermally stable ionic salts (up to 800°C for some cations) and water insoluble covalent salts with heavy metals (29). With non-toxic cations, their salts are non-toxic.

2. Substitution Reactions

a) Initial investigations; oxidations

Wiesboeck, et. al. (30), reported the first reactions of $B_{10}H_{10}^{2-}$, with products reported as $B_{14}H_{12}NO\,[NH(C_2H_5)_3]_2$, $B_{10}H_6(NO)_2 \cdot N(CH_3)_4$, and $B_{10}H_4\,(NO)_3 \cdot N(CH_3)_4$. These products were classed as oxazahydroborates. No subsequent work appeared on these compounds, but Wiesboeck did report in a subsequent paper (30A) that nitrosohydroborates of the type $B_{20}H_{18}NO^{3-}$ did result from treatment of $B_{10}H_{10}^{2-}$ with nitric oxide and ferric ion, and that it was probable that an intermediate involving substituted decahydrodecaborate ion formed before dimerization since $B_{20}H_{18}^{2-}$ did not react with NO_2 or HONO.

Lipscomb and coworkers (1,19.31) early reported a series of unusual reactions for $B_{10}H_{10}^{2-}$. In one case (1) they observed that

$$K_2B_{10}H_{10}(s) + CuCl_2 \xrightarrow[\text{solvent}]{\text{polar organic}} (B_{10}H_x^{2-})_n \qquad \text{(i)}$$

where the product was purple and had free radical characteristics. No further work has appeared on this. It was also reported (1) that reaction of hydroxide ion with $B_{20}H_{18}^{2-}$ gave $B_{10}H_9OH^{2-}$, however, Hawthorne, et. al. (32), showed that the product was actually $B_{20}H_{17}OH^{4-}$.

Lipscomb's group had also postulated that oxidation of $B_{10}H_{10}^{2-}$ with Fe^{3+} or Ce^{4+} gave $B_{20}H_{19}^{3-}$ or $B_{20}H_{18}^{2-}$ where some sort of B-H-B or B-B bridging occurred between two polyhedra (19,31). Thus two isomeric substances of formula $B_{20}H_{18}^{2-}$ were prepared, supposedly involving different bridging arrangements. Hawthorne, et. al. (33) found that the Ce^{4+} oxidation gave a double salt, $B_{20}H_{18}^{2-} \cdot B_{20}H_{19}^{3-} \cdot 5(C_2H_5)_3NH^+$, where the first anion portion was identical to the product of Fe^{3+} oxidation of $B_{10}H_{10}^{2-}$. Further, Hawthorne, et. al. (34) showed that the $B_{20}H_{18}^{2-}$ species involved two B_{10} cages linked through three-center B-B-B bridges. Several forms of $B_{20}H_{18}^{4-}$ and $B_{20}H_{19}^{3-}$ were also characterized (34).

Chamberland and Muetterties (35) have prepared a series of derivatives of $B_{20}H_{18}^{2-}$ by oxidizing $B_{10}H_9L^-$ derivatives, as:

$$2B_{10}H_9L^- + Ce^{4+} \xrightarrow{H^+} B_{20}H_{16}L_2 + 4e^- + Ce^{2+} \qquad \text{(ii)}$$

where for L; $-S(CH_3)_2$, $-IC_6H_5$, $-O{=}\overline{C(CH_2)_3N}(CH_3)$, and $-S(CH_2)_4$

were used, and the IR spectra showed no B-H-B stretch bands.

Kaczmarczyk, et. al. (36) have found also that the ions $B_{10}H_{10}^{2-}$, $B_{12}H_{12}^{2-}$, $B_{20}H_{18}^{2-}$, $B_{20}H_{18}^{4-}$, and $B_{20}H_{17}OH^{4-}$ may be qualitatively oxidized to boric acid with permanganate ion, with $B_{10}H_{10}^{2-}$ the most facile, and $B_{12}H_{12}^{2-}$ the least. At pH 5 to 7,

$$B_{10}H_{10}^{2-} + 14MnO_4^- + 18H_2O \longrightarrow 10B(OH)_4^- + 6OH^- + 14MnO_2\,(s) \qquad \text{(iii)}$$

Polyhydroxylation was proposed as the mechanism.

b) Halogenation and subsequent reactions

Muetterties group (27,29,37) has investigated the preparation and properties of polyhalogenated B_{10} and B_{12} derivatives. The halogenations proceed readily with aqueous or alcoholic solutions of pure halogen or HX, forming isolable crystalline salts or hydrated acids. The B-X bonds are thermally stable and are unaffected by refluxing solutions of OH^- or OCH_3^-. Rate of halogenation is $F_2 > Cl_2 > Br_2 > I_2$, initially rapid and slowing with increasing substitution. Fluorine derivatives, for example, may be prepared as:

$$B_{12}H_{12}^{2-} + HF \longrightarrow B_{12}H_8F_4^{2-} + B_{12}H_7F_5^{2-} + B_{12}H_6F_6^{2-} \qquad \text{(iv)}$$

$$B_{12}H_6F_6^{2-} + F_2 \xrightarrow[\text{aq.}]{0^\circ} B_{12}F_{11}OH^{2-} + BF_4^- \qquad \text{(v)}$$

$$B_{12}H_{12}^{2-} + F_2 \longrightarrow B_{12}F_{11}OH^{2-} \quad \text{(with extreme care)} \qquad \text{(vi)}$$

but evidently $B_{10}H_{10}^{2-}$ reacts too violently, with degredation (29). Other halogens with both anions give up to perhalogenated derivatives, and some twenty-six haloborates were prepared (29). Both electrophilic and free radical substitution mechanisms were invoked. It was also observed that for iodination, the slowest reaction, the product ratio of 1,7-$B_{12}H_{10}I_2^{2-}$ to the 1,12- isomer of 5:1 agreed with Lipscomb's predictions (25) only if I was an electron withdrawing substitutent. No correlations were found for the other halogenations.

Degradation of $(H_3O)_2B_{10}Cl_{10}\cdot 5H_2O$ was observed (37) upon heating, as:

$$(H_3O)_2B_{10}Cl_{10}\cdot 5H_2O \underset{}{\overset{150^\circ}{\rightleftharpoons}} (H_3O)_2B_{10}Cl_{10}\cdot 2H_2O \xrightarrow{260^\circ} \underset{\text{I (red)}}{B_9Cl_8H} \qquad \text{(vii)}$$

and hydrolysis of (I) yields $B_9Cl_8H^{2-}$.

A curious reaction yielding a halogen-boron bond has been reported by Miller, et. al. (41) from reaction of $B_{10}H_{10}^{2-}$ and iodosobenzene under neutral conditions, with no hydrogen evolution:

$$B_{10}H_{10}^{2-} + C_6H_5IO \longrightarrow 1\text{-}B_{10}H_9IC_6H_5^- + OH^- \qquad \text{(viii)}$$

where the cesium salt was recrystallizable from water. The reaction was said to be similar to that of $(CH_3)_2SO$ with $B_{10}H_{10}^{2-}$, in mechanism.

c) Behavior of salts and acids

Muetterties, et. al. (5) have found the observed stability of the two anions to strong acids and bases to be largely kinetic, for the two anions are thermodynamically unstable with respect to boric acid or boric oxide. Large univalent cations (e.g. Ag^+) form insoluble salts without cation reduction, while smaller or more highly charged cations form soluble hydrated salts. The salts are unusually thermally stable (e.g. $Cs_2B_{10}B_{10}$ dec. >600°C, $Cs_2B_{12}H_{12}$ dec. >810°C, sealed evacuated tube). Hydrated acids of the ions are comparable to H_2SO_4, and $K_{a1} < 16K_{a2}$. Since pyridine derivatives of

$B_{10}H_{10}^{2-}$ salts are yellow (charge transfer band) while these derivatives of $B_{12}H_{12}^{2-}$ salts are colorless, it is probable that for electron donor properties, $B_{10}H_{10}^{2-} > B_{12}H_{12}^{2-} \approx I^-$ (5).

d) Diazonium and carbonyl derivatives

The preparation of these derivatives by Knoth, et. al. (28) gave strong evidence that the chemistry of these two anions is at least as extensive as that of aromatic hydrocarbons. Thus,

$$B_{10}H_{10}^{2-} \xrightarrow[\text{aq. } H^+]{NaNO_2} \text{(intermediate)} \xrightarrow[CH_3OH]{NaBH_4} \underset{II}{1,10\text{-}B_{10}H_8(N_2)_2} \quad \text{(ix)}$$

$$1,10\text{-}B_{10}H_8(N_2)_2 + CO \xrightarrow[120^\circ]{\text{no solvent}} \underset{III}{1,10\text{-}B_{10}H_8(CO)_2} \quad \text{(x)}$$

$$1,10\text{-}B_{10}H_8(N_2)_2 \xrightarrow[C_6H_{12}]{CO} \underset{IV}{C_6H_{11}B_{10}H_7\text{-}1,10\text{-}(N_2)_2} + \underset{V}{(C_6H_{11})_2B_{10}H_6^-\ 1,10\text{-}(N_2)_2} \quad \text{(xi)}$$

$$B_{12}H_{12}^{2-} + CO \xrightarrow{H^+} \underset{VI}{B_{12}H_{11}CO^-} + \underset{VII}{B_{12}H_{10}(CO)_2} \quad \text{(xii)}$$

and the product (VII) undergoes an unusual reaction with water,

$$VII + H_2O \rightleftharpoons H^+, B_{12}H_{10}(COOH)CO^- \xrightleftharpoons{H_2O} (H^+)_2, B_{12}H_{10}(COOH)_2 \quad \text{(xiii)}$$

The observed derivative chemistry was very broad (28):

$$1,10\text{-}B_{10}H_8(CO)_2 + \begin{cases} 2CH_3OH \rightleftharpoons (H^+)_2, 1,10\text{-}B_{10}H_8(COOCH_3)_2^{2-} \\ 4NH_3 \longrightarrow (NH_4^+)_2, 1,10\text{-}B_{10}H_8(CONH_2)_2^{2-} \\ LiAlH_4 \longrightarrow 1,10\text{-}B_{10}H_8(CH_3)_2^{2-} \\ NaN_3 \longrightarrow 1,10\text{-}B_{10}H_8(NCO)_2^{2-} \\ H_2NOSO_3H \longrightarrow 1,10\text{-}B_{10}H_8(NH_3)_2 + 2CO_2 \end{cases} \quad \text{(xiv)}$$

Similar reactions occurred with $B_{12}H_{10}(CO)_2$ and $B_{10}Cl_8(CO)_2$. The parent carbonyls are fairly thermally stable, e. g., $B_{10}H_8(CO)_2$ unchanged after two hours at 200°C, $B_{12}H_{10}(CO)_2$ unchanged after one hour at 300°C. (28)

A second method for carbonyl preparation using oxalyl chloride was found by Hertler, et. al. (38),

$$2\text{-}B_{10}H_9N(CH_3)_3 + (COCl)_2 \xrightarrow{CH_3CN} \underset{\text{VIII - 57\% + 2,4-VIII (30\%)}}{2,7(8)\text{-}(CH_3)_3NB_{10}H_8CO} \quad \text{(xv)}$$

and reaction of (VIII) with $NH_2OSO_3^-$ followed by methylation gave the reaction

$$VIII + NH_2OSO_3^- \longrightarrow (CH_3)_3NB_{10}H_8NH_3 \xrightarrow[OH^-]{(CH_3)_2SO_4} \underset{IX}{B_{10}H_8[N(CH_3)_3]_2} \quad \text{(xvi)}$$

and the product (IX) contained the two isomers 2,7(8)- and 2,4-IX in the same ratio as in (VIII). Resolution of (VIII) gave: (+)2,7(8)- $[\alpha]_D = +22°$; (-)2,7(8)- $[\alpha]_D = -14°$ (38,39). When an identical reaction to (xv) was run, using the $B_{12}H_{12}^{2-}$ derivative (38),

$$B_{12}H_{11}N(CH_3)_3^- + (COCl)_2 \xrightarrow{CH_3CN} \underset{X}{(CH_3)_3NB_{12}H_{10}CO} \xrightarrow[2.\ (CH_3)_2SO_4]{1.\ NH_2OSO_3^-} \underset{XI}{[(CH_3)_3N]_2B_{12}H_{10}} \quad \text{(xvii)}$$

where (X) was a low yield mixture of the 1,12- and 1,7- isomers, with no change in relative amounts on conversion to (XI), (38). Carbonylation of an inner sulfonium derivative of $B_{10}H_{10}^{2-}$ proceeded as:

$$1\text{-}B_{10}H_9S(CH_3)_2^- + (COCl)_2 \xrightarrow{CH_3CN} \underset{XII}{1,6\text{-}(CH_3)_2SB_{10}H_8CO} \quad \text{(xviii)}$$

and subsequent reactions for (XII) were as follows. (38)

$$XII + \left\{ \begin{array}{l} NH_2OSO_3^- \longrightarrow 1,6\text{-}(CH_3)_2SB_{10}H_8NH_3 \\ H_2O_2 \xrightarrow{OH^-} 1,6\text{-}(CH_3)_2SB_{10}H_8OH^- \\ (CH_3)_4NCl \xrightarrow{HOH} (CH_3)_4N\,[1,6\text{-}(CH_3)_2SB_{10}H_8COOH] \\ HONO \xrightarrow{H^+} \text{yellow prec.} \xrightarrow[HCl]{Zn} \underset{XIII}{1\text{-}(CH_3)_2SB_{10}H_7\text{-}6\text{-}COOH\text{-}10\text{-}N_2} \end{array} \right. \quad \text{(xix)}$$

Derivative chemistry was employed to determine stereochemistry. The product (XIII) exhibited a pK_a of 8, even with two cationic groups on the cage. The equatorial substitution on the product of (xviii) was contrary to prediction (25). Replacement of N_2 in (XIII) could be effected with pyridine, although the carboxyl group was also converted to (1) -COCl, (2) -NCO, and (3) $-NH_2$ without affecting the N_2 unit.

e) Formation of -O, -N, and -S bonded groups, in general; alkene addition

(1) Groups bonded through oxygen

Knoth, et. al. in an early paper (27), had noted that reaction of benzoyl chloride with $B_{10}H_{10}^{2-}$ gave $B_{10}H_9COC_6H_5$ while a similar reaction with $B_{12}H_{12}^{2-}$ gave only $B_{12}H_{10}(OH)_2^{2-}$. In an extension of the attempt to form a B-C bond with the B_{12} cage, Knoth, et. al. (40), used as a benzoylating agent benzoyl-p-toluene sulfonate (BpTS), but again oxygen bonding was obtained.

$$C_6H_5C(O)OSO_2\text{-}C_6H_4\text{-}p\text{-}CH_3 + B_{12}H_{12} \xrightarrow{CH_3CN} B_{12}H_{11}OCH_2C_6H_5 \quad \text{(xx)}$$

An electrophilic $C_6H_5CO^+$ was postulated as responsible for the product.

However, the authors found (40) that both anions readily formed B-O bonds upon reaction with ethers, alcohols, formaldehyde, ketones, and organic acids, all under acidic conditions. Thus, for example,

$$B_{12}H_{12}^{2-} + \begin{cases} ROH \text{ (primary alcohols)} \xrightarrow{H^+} B_{12}H_{11}(OR)^{2-} \\ ROR \text{ (ethers)} \xrightarrow{H^+} B_{12}H_{11}(OR)^{2-} \\ R_2C{=}O \text{ (ketones)} \xrightarrow{H^+} B_{12}H_{11}OCHR_2 \end{cases} \qquad \text{(xxi)}$$

and disubstitution may also result. If amides are used, say, with $B_{10}H_{10}^{2-}$,

$$B_{10}H_{10}^{2-} + HC(O)N(CH_3)_2 \xrightarrow[HOH]{H^+} \underset{XIV}{B_{10}H_9OCHO^{2-}} + \underset{XV}{B_{10}H_9N(CH_3)_2H^-} \qquad \text{(xxii)}$$

whereas in nonaqueous media with acid catalysis,

$$B_{10}H_{10} + HC(O)N(CH_3)_2 \xrightarrow{H^+} \underset{XVI}{B_{10}H_9OCH{=}N(CH_3)_2} \qquad \text{(xxiii)}$$

and (XIV) and (XVI) may both be converted to $B_{10}H_9OH^-$ in aqueous base, while (XV) gives no reaction, even with the amine proton. Thus this product ion (XV) should be a stronger base than OH^-. The amine proton does exchange with D_2O however (40).

Miller, et. al. (41), reported other B-O compounds formed from reaction of either polyhedral anion with sulfones, amides, tetramethylurea, and nitrobenzene derivatives. The major isomers of $B_{10}H_8L_2^{2-}$ produced appeared to derive from a $B_{10}H_9L^-$ species which was equatorially substituted, and often this was the sole mono-substituted intermediate.

(2) Groups bonded through sulfur

Knoth and coworkers (42,43) have studied the formation of B-S bonds, and their subsequent reactivities, first using thioethers,

$$(H_3O)_2B_{12}H_{12} + (CH_3)_2S \longrightarrow B_{12}H_{11}SCH_3^{2-} + B_{12}H_{10}(SCH_3)_2^{2-} \qquad \text{(xxiv)}$$

where transmethylation with trimethyl sulfonium iodide gave $B_{12}H_{11}S(CH_3)_2^-$ and $B_{12}H_{10}[S(CH_3)_2]_2$ respectively (40), identical with the products of the reaction of B_2H_6 with $(CH_3)_2S$ (15). Similar results were obtained for $B_{10}H_{10}^{2-}$.

Later work on $B_{10}H_{10}^{2-}$ was done with dimethyl sulfoxide (42),

$$B_{10}H_{10}^{2-} + (CH_3)_2SO \xrightarrow{DMSO} \underset{XVII}{B_{10}H_9S(CH_3)_2^-} + \underset{XVIII}{B_{10}H_8[S(CH_3)_2]_2} \qquad \text{(xxv)}$$

with the product ratio dependent on reaction time. If

acetic acid was used as solvent, only (XVIII) resulted, and this was largely 1,10-isomer, with some 1,6-isomer. Metallation of (XVIII) with n-butyl lithium occurred only on the methyl groups, and no deuterium exchange could be forced. The other product (XVII) did exchange with D_2O under forcing conditions, and it could be further reacted with HONO to give 1,10-$(CH_3)_2SB_{10}H_8N_2$ and 1,10-$(CH_3)_2B_{10}H_8NO^-$.

On the other hand, by starting with mono-substituted B_{10} derivatives and DMSO, a variety of products were obtained (42):

$$(CH_3)_2SO + \left\{\begin{array}{l} 2\text{-}B_{10}H_9N(CH_3)_3^- \xrightarrow{H^+} 1,2\text{-, } 1,6\text{-, and } 2,7(8)\text{-}(CH_3)_2SB_{10}H_8N(CH_3)_3 \\ B_{10}H_9COC_6H_5^{2-} \xrightarrow{H^+} (CH_3)_2SB_{10}H_8COC_6H_5^- \\ 2\text{-}B_{10}H_9OCH{=}NH(CH_3)_2 \xrightarrow{H^+} 1\text{-}(CH_3)_2SB_{10}H_8\text{-}6\text{-}OCH{=}NH(CH_3)_2 \\ \left.\begin{array}{l} 2\text{-}B_{10}H_9OCHO^{2-} \\ 2\text{-}B_{10}H_9OH^{2-} \\ 1\text{-}(CH_3)_2SB_{10}H_8\text{-}6\text{-}OH^- \end{array}\right\} \longrightarrow 1\text{-}(CH_3)_2SB_{10}H_8\text{-}6\text{-}OS(CH_3)_2 \end{array}\right.$$

Also, it was noted that mono-S-substituted $B_{10}H_{10}^{2-}$ was less susceptible to halogenation than the parent species. Further, $B_{12}H_{12}^{2-}$ failed to react with DMSO (42).

Finally, the authors observed (42) that treatment of 1,6-$(CH_3)_2SB_{10}H_8NH_3$ with certain aldehydes yielded Schiff bases, e.g., 1-$(CH_3)_2SB_{10}H_8$-6-NH=CH-C_6H_4-Cl.

(3) Groups bonded through carbon

Knoth's group (40) has observed the addition of the polyhedral anions across the double bond of alkenes such as propene and styrene, under acidic conditions. Thus, with styrene, for example, disubstituted $B_nH_{n-2}(C_8H_9)_2^{2-}$ was obtained, with position isomerism, for n = 10 or 12.

(4) Groups bonded through nitrogen

Numerous reactions yielding B-N bonding have been reported. For example, Knoth's group (40) reported that N-methyl pyrrolidone (NMP) forms substitution products with either ion, e. g.,

$$B_{10}H_{10}^{2-} + \text{NMP} \xrightarrow[180^\circ]{H^+} B_{10}H_9(\text{NMP})^- + B_{10}H_8(\text{NMP})_2 \qquad \text{(xxvii)}$$

and the products undergo conventional basic hydrolysis.

Hertler and Raasch (43) were able to aminate both anions with hydroxylamine-O-sulfonic acid,

$$B_{10}H_{10}^{2-} + H_2NOSO_3^- \longrightarrow 2\text{-}B_{10}H_9NH_3^- \xrightarrow{\text{x.s.}} 2,3\text{- and } 2,4\text{-}B_{10}H_8(NH_3)_2$$

$$B_{12}H_{12}^{2-} + H_2NOSO_3^- \longrightarrow 1\text{-}B_{12}H_{11}NH_3^- \xrightarrow{\text{x.s.}} 1,12\text{- and } 1,7\text{-}B_{12}H_{10}(NH_3)_2 \qquad \text{(xxviii)}$$

without catalyst at pH7. The attacking species was probably not NH_2^+ (43).

Hertler (44) has also reacted the electrophilic Vilsmeier reagent with both anions,

$$B_{10}H_{10}^{2-} + CHCl{=}N(CH_3)_2 \longrightarrow \underset{XIX}{2,7(8)\text{-}B_{10}H_8[N(CH_3)_2CH_2Cl]_2} \quad \text{(xxix)}$$

The chlorines in (XIX) were subsequently inert to nucleophiles, perhaps because of the proximate cationic N atom, but they were reducible, yielding $2,7(8)\text{-}B_{10}H_8[N(CH_3)_3]_2$.

Hawthorne and Olsen have characterized the azo coupling reaction of $B_{10}H_{10}^{2-} + ArN_2^+$ (45,46). The products were reported as highly colored dyes. Thus,

$$p\text{-}BrC_6H_4N_2^+,BF_4^- + B_{10}H_{10}^{2-} \xrightarrow[-35°]{CH\ CN} \xrightarrow{\Delta \text{ to R.T.}} \xrightarrow[(CH_3)_4N^+,Cl^-]{H^+} \quad \text{(xxx)}$$

$$C_{10}H_{26}N_3B_{10}Br \xrightarrow{OH^-} C_{14}H_{37}N_4B_{10}Br$$

The former product was characterized as the tetramethylammonium salt of the monoprotonated azo coupling product, with evidence that the extra hydrogen was on nitrogen (46), so $p\text{-}BrC_6H_4\text{-}\underset{H}{N}{=}N\text{-}B_{10}H_9^-,N(CH_3)_4^+$. The latter product was identical, except for having the proton removed by base, so that it contains two $N(CH_3)_4^+$ ions. Other reactions yielded similar products with substitution on the benzene ring of $p\text{-}CH_3^-$, $p\text{-}CH_3O\text{-}$, $p\text{-}NO_2\text{-}$, $m\text{-}NO_2\text{-}$, $m\text{-}CH_3O\text{-}$, and $m\text{-}CF_3\text{-}$. The $B_{10}H_{10}^{2-}$ cage was always apically substituted.

Reaction of either polyhedral anion with sulfonamides or nitrile derivatives yields B-N bonded derivatives of the type $B_nH_{n-1}L^-$ and $B_nH_{n-2}L_2$, according to Miller, et. al. (41). In this case, the $B_{10}H_9L^-$ derivative showed a preference toward apical substitution.

f) Miscellaneous reactions

In general, it has been found that these two anions are remarkably inert toward nucleophilic substitution for hydrogen, except when the reaction is accompanied by acid catalysis. Some displacement by OH^- of oxygen, nitrogen, and sulfur bonded groups has been noted, however. Also, the polyhalogenated species are inert to nucleophilic substitution.

Trofimenko and Cripps (47) have found the polyhalogenated derivatives of the polyhedral anions to be unstable to photolytically catalyzed nucleophilic displacement at B-X bonds.

$$B_{12}Br_{12}^{2-} + 9CN^- \xrightarrow[4\text{ days}]{h\nu} B_{12}Br_3(CN)_9^{2-} + 9Br^-$$

$$B_{12}Cl_{12}^{2-} + 7CN^- \xrightarrow[4\text{ days}]{h\nu} B_{12}Cl_5(CN)_7^{2-} + 7Cl^- \quad \text{(xxxi)}$$

however

$$B_{10}Cl_{10}^{2-} + CN^- \xrightarrow[4\text{ days}]{h\nu} B_{10}Cl_9CN^{2-} + B_{10}Cl_8(CN)_2^{2-} + B_{10}Cl_7(CN)_3^{2-} \quad \text{(xxxii)}$$

The advantage of this process is that it yields greater than di-substitution, as ordinarily found for electrophilic substitution. The sterochemistry of $B_{10}Cl_8(CN)_2^{2-}$ was not established, but its IR spectrum was quite different from 1,10-$B_{10}Cl_8(CN)_2^{2-}$ from electrophilic processes. The reactivity of $B_{10}Cl_{10}^{2-}$ and $B_{12}Cl_{12}^{2-}$ appeared to be the inverse of that found for electrophilic substitution. Other anions, e.g. N_3^- and OCN^- substituted similarly to CN^- (47).

g) Polyhedral rearrangements

Hertler, et. al. (48), in an attempt to ascertain whether polyhedral rearrangements could occur during substitution reactions, have studied the behavior of $B_{10}H_8[N(CH_3)_3]_2$, (1), $B_{12}H_{10}[N(CH_3)_3]_2$, (2) and $B_{10}H_8(CN)_2^{2-}$, (3) at melt temperatures. All five isomers of (1) isomerized at 300° C (melt) to identical mixtures of isomers. Similar results were observed for (3), at 350-500° C. However, (2) underwent only slight isomerization, with decomposition, in melt. No appreciable rearrangements occurred for any of these species below melt temperatures.

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TRANSITION METAL COMPLEXES OF DITERTIARY PHOSPHINES

Ieva O. Hartwell October 12, 1965

INTRODUCTION

The increased stability of complexes involving bidentate ligands over those of the corresponding monodentate ligands is well known (1). In Group VA, the nitrogen containing bidentate ligands were the first to be used in preparing complexes with the discovery of ethylenediamine complexes of platinum and cobalt by Jörgensen in 1889 (2). The synthesis of o-phenylenebis (dimethylarsine) by Chatt and Mann in 1939 (3) led to the preparation and study of many different ditertiary arsine complexes (4). The enhanced stability of the diarsine complexes over the monoarsine complexes led to the first preparation and study of bis (diphenylphosphino)-ethane (Fig. 1 b) complexes by Wymore and Bailar in 1956 (5). Since then Chatt and his coworkers have been the major contributors to the systematic study of this and other ditertiary phosphine ligands. These ligands form complexes with the metal in normal oxidation states and also stabilize low and high oxidation states. The wide range of complexes prepared are illustrated by the tabulation in the abstract.

THEORY

Probably the most important factor in the stabilization effect of diphosphine ligands is their ability to participate in d_{π}-d_{π} bonding. Evidence for this is given by Chatt and Hart (12,13).

The relatively high electronegativity of the diphosphine ligands is also instrumental in the stabilization of low oxidation states (7). This and the "electroneutrality principle" proposed by Pauling (8) have led to the formation of some complexes with a previously unobserved coordination number (5,9,10).

Because the diphosphines exert strong ligand fields to form spin-paired complexes, many of the coordination numbers of complexes can be explained by the "nine-orbital rule", an extention of the "inert-gas rule" for metal carbonyls, first evoked for the diarsine complexes (11).

METHODS OF PREPARATION

Three good methods for the preparation of zero-valent metal complexes have been reported (13,14.20). There are also a number of methods for preparing complexes with the metal in other oxidation states (5,22,23).

METAL COMPLEXES OF THE DITERTIARY PHOSPHINES

The complexes formed by the ditertiary phosphine ligands with various transition metals are summarized in Tables I through VI. For simplicity of presentation the letters and corresponding formulae for the phosphines illustrated in Figure 2 are employed. The discussion below will be confined to the more significant information about each group. In the discussion L is used to designate all of the diphosphine ligands.

A. Groups IVB and VB (Ti and V)

Although the "nine-orbital rule" predicts 8-coordinated Ti(IV), only 6-coordinated complexes of the type $[TiCl_4L]$ have been isolated (17,18). The only reported vanadium complexes are of the type $[VL_3]$ (19,20).

B. Group VIB (Cr,Mo,W)

Complexes of the type $[ML_3]$ (19-21) and substituted carbonyl complexes of the types $[M(CO)_4L]$, $[M(CO)_2L_2]$ and $[M_2(CO)_6L_3]$ (14,24,25) have been extensively studied. Cis and trans isomerism has been observed for the $[Cr(CO)_2L_2]$ derivatives (14).

C. Group VIIB (Mn,Re)

Various mono- and dinuclear complexes of Mn(0) (27,28) and Mn(I) (22,27,29,30) have been studied.

Rhenium complexes have been prepared in the II, III, and V oxidation states (31,32). $[Re^{(V)}OCl_3L]$ is an example of a diamagnetic spin-paired d^2 complex (31).

D. Group VIII

1. (Fe,Ru,Os)

$[RuL_2]$ has been shown to exhibit a unique tautomerism involving a H atom of a methyl group in a tertiary phosphine ligand as shown in Fig. 1 (33).

Fig. 1

By far the most research in this group has been done on the M(II) complexes which are of the type $[MXYL_2]$ (33-42). Cis and trans isomers have been separated for many cases, usually by chromatography (41).

Substituted carbonyl complexes have been reported for Fe(0) (43,44) and Fe(II) (44).

$[Fe(NO)_2L]$ are examples of 4-coordinate d^{10} Fe(-II) (43,47).

2. (Co)

Complexes of Co(0) (20,45), Co(I) (23,27), Co(II) (5,9), and of Co(III) (5,9) have been reported.

3. (Ni,Pd,Pt)

Complexes of M(0) and M(II) have been studied for this group. Although the "nine-orbital rule" predicts 4-coordination for the former and 5-coordination for the latter, both of these coordination numbers have been observed for both oxidation states. $[MX_2L]$ (5,9,10,48,49,54-57,78,79) and [NiXYL] (57,58) are all 4-coordinate. $[MX_2L_2]$ (5,9,10,50-53,59,77) are 4-coordinate except for $[NiX_2L_2]$ (X= Br,I) which are 5-coordinate (10,50,51). $[ML_2]$ (5,13,45,50,52,59) are all 4-coordinate except for [PdIL'] (L= bidentate phosphine, L'= tridentate phosphine) which seems to be 5-coordinate (52).

P^{31} NMR has been used on some diphosphine-carbonyl nickel (0) complexes to determine if the diphosphine is monodentate, chelating, or bridging a dinuclear species (60,61).

E. Group IB (Cu,Ag,Au)

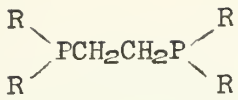
Numerous attempts have been made to resolve the tetrahedral M(I) and M(III) complexes of this group, but they have all failed (65,66). However, in this study a unique 3-coordinate complex [LAuI] was isolated (65).

F. Group IIB (Zn,Cd,Hg)

The tetrahedral complexes of the type $[MLX_2]$ (X= halogen) (5,9,67) and $[MR_2L]$ (R= alkyl, aryl) (68,69) have been reported.

CONCLUSION

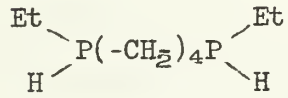
This seminar has shown the versitility of the diphosphine ligands in stabilizing many different kinds of transition metal complexes. Even though the tables show many complexes, there are still many areas to explore. In particular, d^1-d^5 complexes with respect to the "nine-orbital rule" should be studied further.

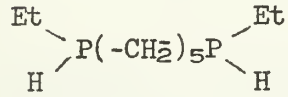


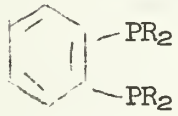
R= a) Me d) $CH_2\emptyset$
b) Et e) CH_2CH_2CN
c) $\emptyset$ f) CF_3
cc) C_6H_{11}

g) $(CD_3)_2PCD_2CD_2P(CD_3)_2$

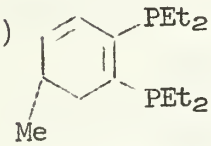
h) $Me_2PCD_2CD_2PMe_2$

i) 

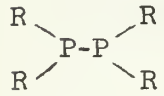
j) 



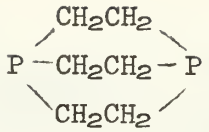
R= k) Me
l) Et
m) $\emptyset$

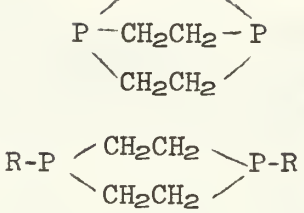
n) 

o) $\emptyset_2PCH_2P\emptyset_2$



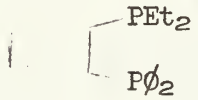
R= p) Me
q) Et
r) $\emptyset$

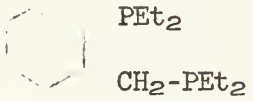
s) 

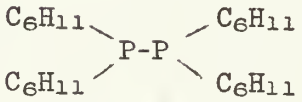


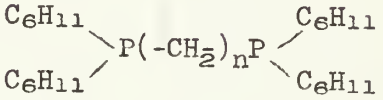
R= t) $CH_2\emptyset$
u) $\emptyset$

v) 

w) 

x) 

y) 

z) 

n= 3,4,5

Fig. 2

TABLE I

d^0 - d^5 Complexes

Complex	Config.	Unpaired electrons	C.N.	Ox. state	References
$[TiCl_4L]$ L= a,b,c,l	d^0	-	6	IV	a,b,1-17; c-18
$[TiCl_3L]$* L= b	d^1	1	5	III	17
$[ReOCl_3L]$ L= b,c	d^2	0	6	V	b-31,32; c-31
$[Re(N\emptyset)Cl_3L]$ L= c	d^2	0	6	V	32
$Y_n[Cr(SCN)_4L]_n$ Y= H,H_2L,Cu,Cd, Zn,Ni,Cs L= b,cc	d^3	1	6	III	80
$[Cr(SCN)_3YL]$ Y= H_2O,py L= b,cc	d^3	1	6	III	80
$[ReCl_3(PEt_2\emptyset)L]$ L, c	d^4	0	6	III	31
$[ReCl_2L_2]Cl$ L= c	d^4	0	6	III	31
$[VL_3]$ L= a	d^5	1	6	0	19,20
$[M(CO)_2L_2]X$ M= Mo,W X= I_3,ClO_4, L= c	d^5	1	6	I	76
$[Cr_2(CO)_8L]$ L= p,q	d^5	0^+	6	I	26
$[M_2(CO)_8L]$ M= Mo,W L= q,r	d^5	0^+	6	I	26
$[(CO)_4Mo\langle^{PMe_2}_{PMe_2}\rangle Mo(CO)_2L$ L= c	d^5	0^+	6	I	75
$[ReCl_2L_2]$ L= c	d^5	1	6	II	31
$[FeCl_2L_2]$ $[FeCl_4]$ L= a,b,m	d^5	1	6	III	36

*Little evidence cited in support of this

+M-M bond accounts for the diamagnetism

TABLE II

d^6 Complexes

Complex	Unpaired electrons	C.N.	Ox. state	References
$[ML_3]$ M= Cr,W L= a	0	6	0	19,20
$[MoL_3]$ L= a,c,l	0	6	0	a-19,20,21; c,l-21
$[M(CO)_4L]$ M= Cr,Mo,W L= b,c,l,o	0	6	0	14,24,25
$[Cr(CO)_2L_2]$ L= c,l,o	0	6	0	c-14,24,25; l,o-14
$[Mo(CO)_2L_2]$ L= c,l	0	6	0	c-14,24,70; l-14
$[W(CO)_2L_2]$ L= c,l	0	6	0	c-14,24; l-14
$[M_2(CO)_6L_3]$ M= Cr,Mo,W L= c	0	6	0	24
$[M_2(CO)_{10}L]$ M= Mo,W L= p,q	0	6	0	26
$[Mn(CO)_3LX]$ L= b X= Br,I	0	6	I	22,27
$[Mn(CO)_2L_2]X$ L= c X= Cl,I, $Mn(CO)_5$ $B\emptyset_4$	0	6	I	27
$[YMn(CO)L]$ Y= *Cp,*MeCp L= c	0	6	I	29,30
$[YMn(CO)_2]_2L$ Y= Cp,MeCp L= c	0	6	I	29,30
$[FeHClL_2]$ L= a,b,l,m	0	6	II	a-34,36; b-34, 36,37; l-34; m-36
$[FeHIL_2]$ L= b	0	6	II	36
$[RuHClL_2]$ L= a,b,l	0	6	II	a-35,38,39,40; b-35,37,38; l-35
$[RuHBrL_2]$ L= a,b	0	6	II	a-35,38; b-35, 37,38
$[RuHIL_2]$ L= a,b,l	0	6	II	a-35,38; b-35, 37,38; l-35
$[RuHXL_2]$ X= SCN, CN L= a,b	0	6	II	a-35; b-35,37
$[RuH(NO_2)L_2]$ L= a	0	6	II	35
$[RuH(\emptyset)L_2]$ L= a	0	6	II	33,39,41
$[RuH(\underline{p}\text{-tolyl})L_2]$ L= a	0	6	II	39,41
$[RuH(2\text{-}C_{10}H_7)L_2]$ L= a,g,h	0	6	II	33
$[RuHYL_2]$ Y= anthryl, phenanthryl, $C_{10}H_6D$ L= a	0	6	II	33
$[RuD(2\text{-}C_{10}D_7)L_2]$ L= a,g	0	6	II	33

*Cp= cyclopentadienyl

[illegible]

TABLE II CONTINUED

Complex	Unpaired electrons	C.N.	Ox. state	References
$[RuHMeL_2]$ L= c	0	6	II	38,39,41
$[RuHRL_2]$ R= Et,Pr^n L= c	0	6	II	38,41
$[OsHClL_2]$ L= a,b,c,o	0	6	II	a,c,o-35; b-34,35,37
$[OsHXL_2]$ X, I,SCN L= b	0	6	II	35,37
$[OsHRL_2]$ R= Me,Et L= c	0	6	II	41
$[FeH_2L_2]$ L= l	0	6	II	34,45
$[RuH_2L_2]$ L= a,b,l	0	6	II	a-33; b,l-35
$[OsH_2L_2]$ L= b,l	0	6	II	35
$[FeCl_2L_2]$ L= a,b,m	0	6	II	36
$[RuCl_2L_2]$ L= a,b,c,l,o	0	6	II	a-38,39,42; b,c,-38,42; l,o-42
$[OsCl_2L_2]$ L= a,b,c,o	0	6	II	42
$[RuBr_2L_2]$ L= a,b,	0	6	II	a-38,39,42; b-38,42
$[RuI_2L_2]$ L= a,b,l	0	6	II	a-38,39,42; b-38,42; l-42
$[OsI_2L_2]$ L= b	0	6	II	42
$[Ru(CN)_2L_2]$ L= a,b	0	6	II	a-39,42; b-42
$[Ru(CAc)_2L_2]$ L= a	0	6	II	42
$[Ru(Me)_2L_2]$ L= a,c,o	0	6	II	41
$[Os(Me)_2L_2]$ L= o	0	6	II	41
$[M(\emptyset)_2L_2]$ M= Ru,Os L= o	0	6	II	41
$[RuClMeL_2]$ L= a,c,o	0	6	II	41
$[OsClMeL_2]$ L= c,o	0	6	II	41
$[MClEtL_2]$ M= Ru,Os L= c,o	0	6	II	41
$[RuClPr^nL_2]$ L= c	0	6	II	41
$[RuClYL_2]$ L= a Y= $\emptyset$,p-tolyl	0	6	II	41
$[RuCl(H_2O)L_2]$ L= l	0	6	II	42
$[RuBrRL_2]$ R= Me,Pr^n L= c	0	6	II	41
$[RuBr(p\text{-tolyl})L_2]$ L= a	0	6	II	41
$[RuBr(2\text{-}C_{10}H_7)L_2]$ L= a	0	6	II	33
$[RuIMeL_2]$ L= a,c	0	6	II	41
$[RuIEtL_2]$ L= c	0	6	II	41
$[RuI\emptyset L_2]$ L= a	0	6	II	41
$[Ru(SCN)MeL_2]$ L= c	0	6	II	41
$[Fe(C_3F_7)IL]$ L= c	0	6	II	44
$[Fe(CF_2)_4(CO)_2L]$ L= c	0	6	II	44
$[Fe(CO)_2Cl_2L]$ L= c	0	6	II	44
$[FeX_2L]$ X= Cl,Br,I,NO_3 L= z	0	4	II	79
$[CoL_2X_2]X$ X= Cl,Br,I L= b	0	6	III	5,9

TABLE III

d^7 Complexes

Complex	Unpaired electrons	C.N.	Ox. state	References
$[Mn(CO)_3L]$ L= c	1	5	0	27
$[Mn(CO)L_2]$ L= c	1	5	0	27
$[Mn_2(CO)_8L]$ L= c	0*	6	0	28
$[Fe_2(CO)_6L]$ L= p,q	0*	6	I	26
$[L(CO)Fe(SR)_2Fe(CO)_3]$ R= Et,Ø L= c	1	5	I	74
$[L(CO)Fe(PMe_2)_2Fe(CO)_3]$ L= c	0*	6	I	75
$[CoL_2I]I$ L= b	1	5	II	5,9
$[CoL_2][CoBr_4]$ L= b	1	4	II	5,9
$[CoX_2L_2]$ X= Br,I L= r‡	1	4	II	77
$[CoBr_2L]$ L= i,j	1	4	II	46
$[CoX_2L]$ X= Cl,Br,I L= y,z	1	4	II	y-78; z-79
$[NiBr_3L]$ L= a,b	1	5+	III	a-10; b-5,9
$[NiBr_2L_2]X$ X= Br,Br_3 L= a	1	6	III	10
$[NiI_2L_2]I$ L= a	1	6	III	10

* M-M bond accounts for diamagnetism; + or octahedral polymer

‡ L is acting as a monodentate ligand

TABLE IV

d^8 Complexes

Complex	Unpaired electrons	C.N.	Ox. state	References
$[FeL_2]$ L= a	0	4	0	20
$[RuL_2]$ L= a,g,h	0	4	0	33
$[Fe(CO)_3L]$ L= c,e	0	5	0	c-43,44; e-43
$[Fe(CO)_4]_2L$ L= c,p	0	5	0	c-30,44; p-26
$[L\text{-}Fe(CO)_3\text{-}L]$* L= c	0	5	0	44
$[CoHL_2]$ L= c	0	5	I	23
$[Co_2(CO)_4L_3]X_2$ X= I,I_3,$[Co(CO)_4]$ $B\emptyset_4$,ClO_4; L= c	0	5	I	27

* L is acting as a monodentate ligand

TABLE IV CONTINUED

Complex	Unpaired electrons	C.N.	Ox. state	References
$[NiCl_2L]$ L= a,b,c,y; z	0	4	II	a-10; b-5,9; c-10,48; y-78; z-79
$[PdCl_2L]$ L= b,c,y	0	4	II	b-9; C-49; y-78
$[NiBr_2L]$ L= a,b,c,y,z	0	4	II	a-10; b-5,57; c-10; y-78; z-79
$[PdBr_2L]$ L= d,n,t,u	0	4	II	d,t,u-53; n-64
$[NiI_2L]$ L= a,z	0	4	II	a-10; z-79
$[M(CNO)_2L]$ M= Pd,Pt L= c	0	4	II	54
$[NiBr_2L_2]$ L= r*	0	4	II	77
$[PdCl_2L_2]$ L= l	0	4 or 6+	II	52
$[PdCl_2L_2]$ L= r*	0	4	II	77
$[PtCl_2L_2]$ L= a,c	0	4	II	59
$[NiBrL]Br$ L= a,c,l,o	0	5	II	a,c,o-10; l-50,51
$[PdL_2]Br_2$ L= c,l	0	4	II	52
$[NiIL_2]I$ L= a,b,c	0	5	II	10
$[NiL_2](ClO_4)_2$ L= b	0	4	II	5,9
$[NiL_2](NO_3)_2$ L= c,l	0	4	II	52
$[PdL_2](NO_3)_2$ L= b	0	4	II	52
$[PdL_2][PdBr_4]$ L= t,u	0	4	II	53
[NiBr(mesityl)L] L= b	0	4	II	57
[NiIRL] R= C_2F_5, n-C_3F_7; L= c	0	4	II	58
$[PdMe_2L]$ L= c	0	4	II	49
$[PtR_2L]$ R= Me,ϕ; L= b	0	4	II	55,56
$[M(SR)_2L]$ M= Ni,Pd; L= c	0	4	II	48
$[LPd<(P\phi_2)_2>PdL]X_2$ X= Cl,ClO_4,$B\phi_4$, picrate, NO_3; L= c	0	4	II	71,72
$[LPd<(P\phi_2)_2>PdL](HgCl_3)_2$ L= c	0	4	II	72
$[LPd<(PO_2)_2>PdL](B\phi_4)_2$ L= c	0	4	II	73
$[LPd<(PEt_2)_2>PdL]X_2$ X= ClO_4,picrate L= c				
$[I_3AuLAuI_3]$ L= b	0	4	III	5,9
$[AuL_2]X_3$ X= Cl,Br,I,ClO_4,picrate L= b,n	0	4	III	65
$[AuI(DMF)L_2](picrate)_2$ ∓ L= b	0	6	III	65

* L is acting as a monodentate ligand; + insoluble in $C_6H_5NO_2$

∓ DMF= dimethylformamide

TABLE V

d^9 Complexes

Complex	Unpaired electrons	C.N.	Ox. state	References
$[CoL_2]$ L= a,l	1	4	0	a-20; l-45

TABLE VI

d^{10} Complexes

Complex	Unpaired electrons	C.N.	Ox. state	References
$[Fe(NO)_2L]$ L= c,e	0	4	-II	c-43,47; e-43
$[NiL_2]$ L= a,c,l,m	0	4	0	a-52; c-13,52; l-13,50,45,52; m-13
$[PdL_2]$ L= a,c,l,o	0	4	0	a,c,o-52; l-45,52
$[PtL_2]$ L= a,c	0	4	0	59
$[PdLL^1]$ L= e; L^1= c,o-$C_6H_4(AsEt_2)_2$ o-$C_6H_4(AsMe_2)_2$	0	4	0	52
$[PdLL^1]$ L= l; L^1= $MeC(CH_2P\emptyset_2)_3$	0	4 or 5 *	0	52
$[Ni(CO)_2L]$ L= a,b,c,e,f,k,l,m	0	4	0	a-10; b-13,50, 60,61; c-13,48 e-60,61,62; f-63; k,m-13; l-13,50,60
$[(CO)_2Ni\langle^{L}_{L}\rangle Ni(CO)_2]$ L= b,e	0	4	0	b-13,60,61; e-60,61
$[(CO)_3Ni\text{-}L\text{-}Ni(CO)_3]$ L= b	0	4	0	60,61
$[CuL_2]$ $[CuLI_2]$ L= b	0	4	I	5,9
$[AgL_2]$ (AgI_2) L= b	0	4	I	5,9
$[AgL_2]X$ X= I,picrate, AgI_2 L= n	0	4	I	65
$[AuL_2]X$ X= I,picrate,NO_3,HSO_4 L= n,v,w	0	4	I	n-64; v,w-65
$(LCuX)_3$ X= Cl,I; L= c	0	?*	I	66
$(LCuX)_2$ X= Cl,Br L= r,y	0	4	I	r-77; y-78
$[LCuBH_4]$ L= c	0	4	I	66
$[LAuX]$ X= Cl,Br,I,picrate L= x	0	3	I	65
$[IAuLAuI]$ L= b	0	2	I	5,9
$[ClAuLAuCl]$ L= s	0	2	I	53
$[MCl_2L]$ M= Zn,Cd; L= c	0	4	II	67
$[MBr_2L]$ M= Zn,Cd; L= b,c	0	4	II	b-5,9; c-67
$[HgBr_2L]$ L= b	0	4	II	5,9
$[HgL(HgCl_2)_2]$ L= c	0	4	II	67
$2CdLBr_2 \cdot CdBr_2$* L= b	0	4	II	5,9
$[ZnR_2L]$ R= C_4H_9,C_6H_5,C_6F_5 L= c	0	4	II	69
$[HgR_2L]$ R= C_6F_5; L= b	0	4	II	68

* Inconclusive evidence

TABLE II

[illegible]

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

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A SURVEY OF THE CO-ORDINATION CHEMISTRY OF AMINE N-OXIDES

David Herlocker October 19, 1965

INTRODUCTION:

Although the first report of a pyridine N-oxide complex appeared in 1948 (1), it has been only in the past few years that amine N-oxides—both aliphatic and aromatic—have found widespread use in co-ordination chemistry. The interest in these compounds as ligands has been a logical extension of the work involving oxidized forms of phosphorus, arsenic, and sulfur donors.

GENERAL STUDIES OF PYRIDINE AND QUINOLINE N-OXIDES:

Quagliano et. al. (2), in reporting the first detailed study of the use of pyridine N-oxide as a ligand, used magnetic moments, changes in the N-O stretching frequency, and conductance data to determine, when possible, the structures of the compounds prepared. The infrared data showed significant reductions in the N-O stretching frequencies upon co-ordination, indicating oxygen co-ordination. The conductance work (done in DMF) is of little use, due to replacement of the ligands by the solvent. Low magnetic moments for octahedral cobalt ($\mu \cong 4.7$ B.M.) and subnormal moments for $CuL_{1 \text{ or } 2}\ Cl_2$ were noted.

Carlin (3) has prepared a series of transition metal perchlorates, obtaining solution spectra in acetonitrile. The spectral data are questionable, in view of the high donor strength of acetonitrile (4). Meek, Drago, and Piper (5) have prepared and assigned spectrochemical parameters to the chromium (in acetone), cobalt, and nickel (in DMF) perchlorate complexes of pyridine N-oxide. The donor strength of the solvent (6) is again expected to cause at least partial dissociation of the latter two complexes.

Carlin and Baker (7) have shown the series $ML_6(NO_3)_2$ and $ML_2(NO_3)_2$ ($M = Mn^{+2}, Co^{+2}, Ni^{+2}$, and Cu^{+2}) —in which the nitrate group is shown to be ionic and bidentate, respectively—to be similar by means of magnetic moment and solid state spectral data. Infrared data were used to determine the presence of ionic and co-ordinated nitrate in the two series of compounds. The co-ordination of the nitrato group in the "bis" series is assumed to be essentially that reported by Cotton and Soderberg (8,9). Spectral data in methanol, ethanol, and acetonitrile are again suspect.

Isslieb and Kreibich (11) have assigned to the compounds CoL_3Br_2 and CoL_3I_2 tetrahedral structures on the basis of magnetic data, molecular weight studies in phenol, and conductance studies in acetonitrile. They have also assigned tetrahedral and octahedral structures, respectively, to $CoL_2(NO_3)_2$ and $CoL_6(ClO_4)_2$. Only the last structure appears to be correct, for Bertrand and Plymale (12) present evidence supporting the structure $[CoL_6]\ [CoX_4]$ in the solid state. Dissolution of the chloro and bromo compounds in DMF and acetonitrile yielded CoX_4^{-2} spectra, but with ligand replacement in the cation. Thus the chloro (2) and bromo (11) (and probably iodo (11)) compounds are similar to those reported (13) for dimethylsulfoxide compounds. The similarity of pyridine N-oxide and quinoline N-oxide as ligands has been demonstrated (14).

A definitive survey of the infrared spectra of many of these compounds has been reported (15,16). The N-O stretching frequency has been shown to decrease upon co-ordination, depending on the oxidation state of the metal and the type of co-ordinated ligands, but the N-O bending frequency is less sensitive. A study in the cesium bromide region (16) indicated M-O stretching frequencies for tripositive ions to be $> 400\ cm^{-1}$ and those for bipositive ones $< 400\ cm^{-1}$. The Irving-Williams stability scheme (17) was observed for the bipositive ions, and it was generally observed that an increase in the M-O stretching frequency was accompanied by a decrease in the N-O stretching frequency.

Utilizing 4-substituted pyridine N-oxides, Carlin et. al. (10) have reported the preparations of the 4-methylpyridine N-oxide complexes of cobalt and nickel perchlorates. Quagliano et. al. (16) have prepared complexes of 3- and 4-acetylpyridine N-oxide with Co^{+2}, Ni^{+2}, Zn^{+2}, and Fe^{+3}. Upon co-ordination a rise in the C=O stretching frequency was observed, the effect being more noticeable in the 4-substituted complexes.

Imhof (18) has studied a series of complexes $M(4\text{-}XpyNO)_6(ClO_4)_n$ ($M = Ni^{+2}, Cr^{+3}$; $X = Me, OMe, Cl, NO_2$), attempting to correlate changes in observable properties of the compounds with changes in the Hammett substituent constants of the X-groups. Correlations of the N-O stretching frequencies for both complexed and free ligands were manifested as plots of σ^+ vs. log ν/ν_0, with ν and ν_0 being the stretching frequencies of the substituted and unsubstituted (2,15,16) ligands, respectively. A correlation was also obtained for the Ni-O stretching frequency. Both ends of the 4-nitro complex were found to act as donor sights, giving rise to dual Ni-O stretching frequencies and a surprisingly high Dq. Dq and B values for these complexes are reported in nitromethane (with added ligand) for these complexes.

Further work (19) has shown these complexes to be stable toward decomposition in nitromethane, provided excess ligand is present. The ligand 4-acetylpyridine N-oxide (16) has been added to those ligands studied previously (18). Hatfield (20) has reported magnetic data for complexes of the type $M(4\text{-}XpyNO)_6(ClO_4)_n$ ($M = Fe^{+3}, Cr^{+3}, Co^{+2}$, and Ni^{+2}; $X = H, NO_2$, Cl, and Me). Hieber and Lipp (21) have prepared FeL_6X ($X = [Fe_4(CO)_{13}]^{-2}$ and $2I^-$), while Isslieb and Kreibich (11) have isolated FeL_2Cl_3, a monomer in phenol, which may be trigonal bipyramidal.

Ramaswamy and Jonassen have reported the tetrahedral complexes CoL_2Cl_2 (L = 2,4-dimethyl and 2,4,6-trimethylpyridine N-oxide). Color, magnetic data, reflectance spectra, and a unique N-O stretching frequency were used in the characterization. Dissolution in co-ordinating solvents yielded six co-ordinated species. A report (11) of MnL_2Br_2 (L = pyridine N-oxide) as tetrahedral complex is unlikely.

Wilkins and Haendler (23) have prepared several adducts of the type SnL_4X_2, with X = halide. The appearance of several Sn-F stretching frequencies is indicative of a cis-structure for the fluoride and probably all of the compounds. An octahedral silicon compound $[Si(OpyNO)_3]^+$ (OpyNO = 2-hydroxypyridine N-oxide has been reported (24,25).

STUDIES INVOLVING SUBNORMAL MAGNETIC MOMENTS OF COPPER COMPOUNDS:

The low magnetic moments reported for the copper compounds (2) have been noted by others (11,14,26,27). Below are tabulated data on these compounds.

Table I

Magnetic Data of Copper Compounds[d]

Compound	Mom. (B.M.)	T(°C)	Ref.	Compound	Mom. (B.M.)	T(°C)	Ref.
$Cu(pyNO)Cl_2$[a]	.85	---	2	$Cu(4\text{-}OHpyNO)Cl_2$	.0	24.8	26[b]
" "	.77	20	14	$Cu(3\text{-}MepyNO)Cl_2$	.39	---	20
" "	1.09	21	26[b]	$Cu(3\text{-}MepyNO)Br_2$	.28	---	20
$Cu(pyNO)_2Cl_2$	.63	---	2	$Cu(2,4\text{-}MepyNO)Cl_2$	.3	---	20
" "	.77	20	14	$Cu(2,4\text{-}MepyNO)Br_2$	.3	---	20
$Cu(pyNO)Br_2$	.65	20	14	$Cu(2,4,6\text{-}MepyNO)Cl_2$	.3	---	20
$Cu(pyNO)_2Br_2$	1.47	21	11[b]	$Cu(2,4,6\text{-}MepyNO)Br_2$	.3	---	20
$Cu(pyNO)_4(ClO_4)_2$	1.62	---	2[c]	$Cu(QuNO)Cl_2$	.36	20	14
$Cu(4\text{-}ClpyNO)Cl_2$	.72	3.6	26[b]	$Cu(QuNO)Br_2$	.40	20	14
$Cu(4\text{-}ClpyNO)Br_2$	.23	24.7	26				
$Cu(4\text{-}MepyNO)Cl_2$	.51	26.4	26[b]				
$Cu(4\text{-}MepyNO)Br_2$	.26	24.8	26				
$[Cu(4\text{-}MepyNO)Br_2)_n$	1.33	24.6	26				

a. PyNO = Pyridine N-oxide and QuNO = Quinoline N-oxide

b. These moments were taken at various temperatures; the value at ≈ 20°C is given whenever possible.

c. This report is the only indication of a subnormal moment for this compound.

d. Jonassen et al. (45) have studied more complexes of this type. No data are yet available, however.

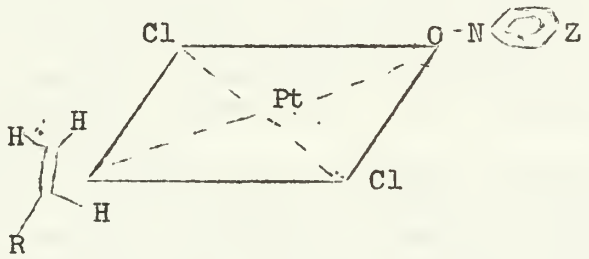
A study of χ vs T (14,27) on $Cu(pyNO)Cl_2$ has shown χ to be independent of $\vec{H}$ but dependent on T. A singlet-triplet separation of ≅ 650 cm^{-1} was found, and it was noted (14,27) that the compound is diamagnetic below 90°K. X-ray work (27) has shown the compound to be a dimer with approximately D_{2d} configurations about each copper (as in $CuCl_4^{-2}$ and $Cu_2Cl_6^{-2}$). A long Cu-Cu distance of 3.23A°—indicating no metal-metal bond—an O-Cu-O angle of 76°, and an O-O distance of 2.51A° indicate considerable interaction between the rings.

From a study of the triplet-singlet energy difference as a function of substituent in $Cu(4\text{-}XpyNO)Cl_2$ (X = H,Me,Cl, and OH), Hatfield and Paschal (28) have found ΔE to be a function of σ_r (with $\sigma_r = \sigma - \sigma_i$, as defined by Taft (29)). While this effect can be explained by postulating a super-exchange mechanism, it can not be explained by invoking a metal-metal bond.

Two N-O stretching frequencies are observed (26) in $Cu(pyNO)_2Cl_2$, and at 85-90° one ligand is lost, with the disappearance of the higher energy band. Replacement of the aforementioned ligand with DMF and DMSO indicates the possibility of a polymeric structure with six co-ordinated copper. No X-ray work has yet been reported on this and other systems (20,26) whose magnetic properties vary with the ligand.

STUDIES OF BONDING IN PLATINUM-OLEFIN COMPLEXES CONTAINING PYRIDINE N-OXIDES:

Orchin and co-workers (30-34) have studied in detail the bonding in substituted Zeise's salts, and have noted the changes in bond properties as a function of the change in the Z-group on the pyridine N-oxide (Fig. 1)



R = X-substituted styrenes, H Figure 1

It was noted that while the Pt-O stretching frequency is insensitive to changes in Z (33), and must thus be essentially covalent with little back bonding, the C=C stretching frequency varies linearly (32) with the Hammett σ- values of the Z substituents. A plot of the N-O stretching frequencies (32) of various substituted N-oxides, both free and complexed, yield curves also showing the small effect of the Pt-O bond on the N-O bond. A study of reactions involving exchange between various substituted m-and p- styrenes and 1-dodecene (34) has shown that the Z-groups on the N-oxides exert a far greater effect on the exchange rates than do the X-groups on the styrenes.

STUDIES OF OTHER AROMATIC N-OXIDES:

Several reports (35-37) have appeared recently on the co-ordination chemistry of 2,2'-bipyridine N,N'-dioxide. The ligand is assumed to exist in complexes in a gauche position (36), similar to ethylenediamine. The compounds formed were generally octahedral, and many held lattice water quite tenaciously (35-7). Conductance data in DMF (37) indicated decomposition of some of the complexes; thus spectral data in this solvent are somewhat suspect. The Irving-Williams series (17) is again followed for the M-O stretching frequencies in bipositive ions for several complexes of this ligand (38); no such pattern is found for the N-O stretching frequency.

The chelate picolinic acid N-oxide has been utilized (39,40) in complexes of Be^{+2}, Ca^{+2}, Mg^{+2}, Cr^{+2}, $Mn^{+2,+3}$, $Fe^{+2,3}$, $Co^{+2,+3}$, Ni^{+2}, Cu^{+2}, and Zn^{+2}. Infrared studies were used to separate the complexes into two groups—one anhydrous group (containing tripositive cations and small, polarizable ones) and one group (containing bipositive cations) with water attached to the metal. A series of $ML_2(H_2O)_2$ compounds was found to be isomorphous, and are assumed to be octahedral in nature. Spectrochemical parameters in methanol or the solid state (40) produced Dq values close to that of water, and B values close to that of cyanide.

STUDIES OF ALIPHATIC N-OXIDES:

The aliphatic ligand most studied, trimethylamine N-oxide (TMNO), has quite different steric properties from those of pyridine N-oxide, the former being isolated mainly in tetrahedral complexes (7,11,19,41), the latter almost exclusively in octahedral complexes.

Isslieb and Kreibich (11) have used molecular weight studies, magnetic data, and conductance data to characterize MnL_2Br_2, CoL_2Br_2, $[CoL_3I]I$, $CoL_2(NO_3)_2$, and $[CoL_4](ClO_4)$ (L = TMNO) as tetrahedral compounds. The perchlorate and nitrate compounds—along with $[CoL_4](NO_3)_2$—were studied by Carlin and Baker (7). It was found that both $[CoL_4](ClO_4)_2$ and $[CoL_4](NO_3)_2$ are tetrahedral (μ = 4.7 B.M.) in both the solid state and acetonitrile solution. The compound $CoL_2(NO_3)_2$ (μ = 4.91 B.M.) was assigned an octahedral structure on the basis of infra red, solid state spectral, and magnetic moment data. It is considered analogous to $Co(Me_3PO)_2(NO_3)_2$ (8,9).

Kida (42), in measuring the infrared spectra of several complexes containing TMNO, has concluded that there is little π-character in the N-O bond and that it is strongly coupled with other stretching and bending modes, thus accounting for its small frequency shift on complexation.

Drago, Donoghue, and Herlocker (41) have reported a series of six complexes—$[ML_4](ClO_4)_2$ (M = Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, and Ni^{+2}) and $[CrL_6](ClO_4)_3$. From conductance, infrared, powder pattern, magnetic moment, and electronic spectral data tetrahedral structures were assigned to the manganese, cobalt, and zinc complexes. The chromium compound is octahedral and the nickel complex distorted tetrahedral, with the copper complex probably having a distorted square planar geometry. Dq and B were reported for the chromium and cobalt complexes in nitromethane. It was noted that solvent co-ordination, with the formation of six co-ordinated species, occurred with the nickel and copper complexes in nitromethane.

Further work (19) has yielded a series of $[CoL_4]X_2$ compounds (X = ClO_4^-, BF_4^-, Tosylate$^-$, NO_3^-, Br^-, and I^-) and a series of CoL_2X_2 compounds (X = Cl^-, Br^-, I^-, and SCN^-). Solid and acetonitrile spectra, magnetic data, conductance data, and nuclear magnetic resonance contact shift data (43) have been used to characterize these compounds. All of the "bis" compounds can be converted to "tetrakis" compounds, by the addition of excess ligand in acetonitrile, with the exception of the chloro compound, which forms $[CoL_3Cl]Cl$.

Summers and Quagliano (44) have studied some complexes of N,N-dimethylethylenediamine N-oxide

$$(Me_2\overset{O}{\overset{\uparrow}{N}}CH_2CH_2NH_2).$$

Its steric properties allow the formation of six-membered rings (boat conformations) in its complexes. For a series of bipositive metal halide and perchlorate complexes, the Irving-Williams order of N-O stretching frequencies is followed. Conductance, solution spectral, infrared, and magnetic moment data were used to characterize the complexes. The Dq of the ligand toward nickel (in DMF) appears to be 980 cm^{-1}.

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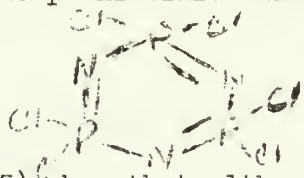
ELECTRONIC STRUCTURE AND BONDING IN PHOSPHONITRILIC DERIVATIVES

John H. Forsberg November 2, 1965

Introduction:

The first structural investigations (1,2,3) on phosphonitrilic derivatives supported Stokes' earlier suggestion (4) that these compounds were cyclic and also definitely established π-bonding in the ring on the basis of observed bond lengths. A typical example of a cyclic derivative is the trimeric-phosphonitrilic-chloride.



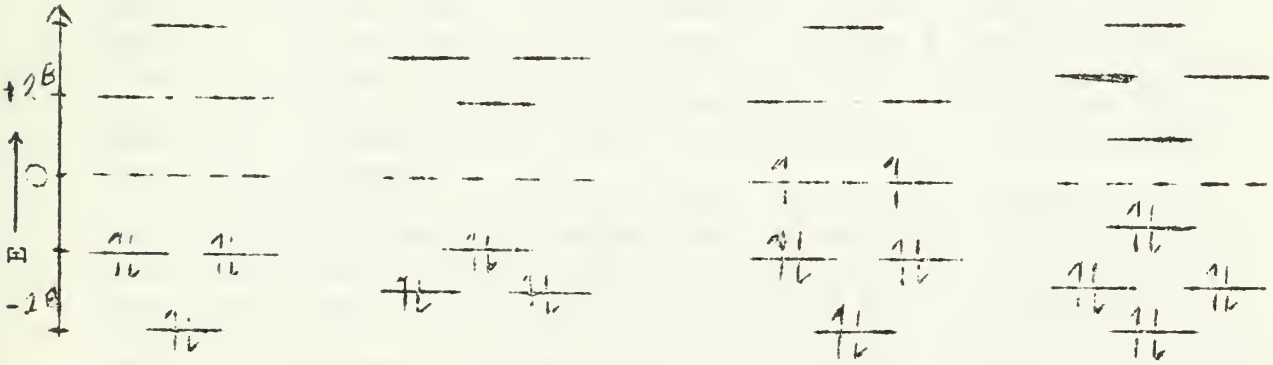
Theoretical studies (5) show that although structures such as I are formally the same as the Kekulé structures of benzene, there is an essential difference, namely, benzene utilizes only p-orbitals in the formation of its π-system, but the phosphonitriles utilize both p and d-orbitals. A phosphonitrile is, therefore, called "a new type of aromatic compound".

The problem of the bonding is more involved in the phosphonitriles because of the wide variety of d-orbitals available and the difference in symmetries of the p and d-orbitals. In this seminar, I shall attempt to ellucidate the current bonding theories by (1) showing the essential differences between the p_π-p_π and p_π-d_π aromatic systems; (2) comparing the relative importance of the various d-orbitals involved in the p_π-d_π overlap; (3) relating the electronic configuration to the possible molecular structures.

COMPARISON OF p_π-d_π AND p_π-p_π SYSTEMS:

The basic differences between p_π-p_π and p_π-d_π bonding can be seen from the results (5,6) of molecular orbital calculations illustrated in figures 1, 2 and 3.

Figure 1



p_π-p_π p_π-d_{xz} p_π-p_π p_π-d_{xz}

SIX MEMBERED RING EIGHT MEMBERED RING

Figure 2

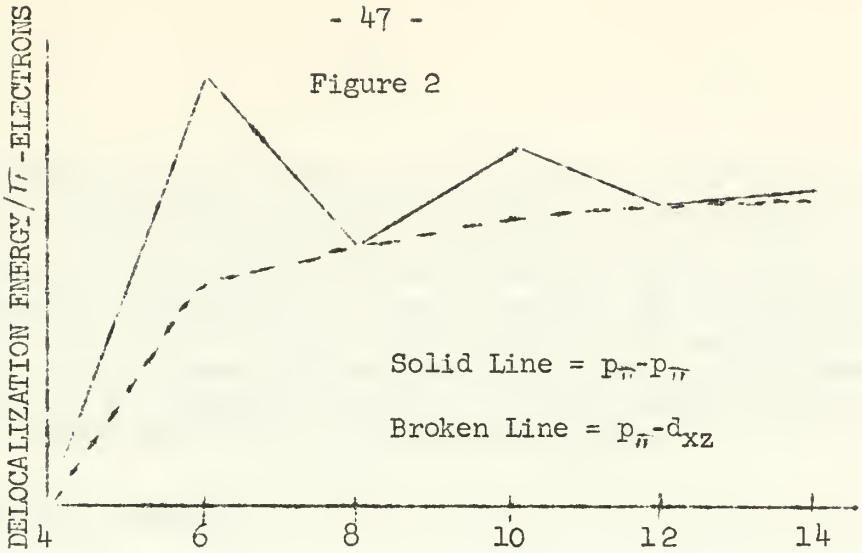
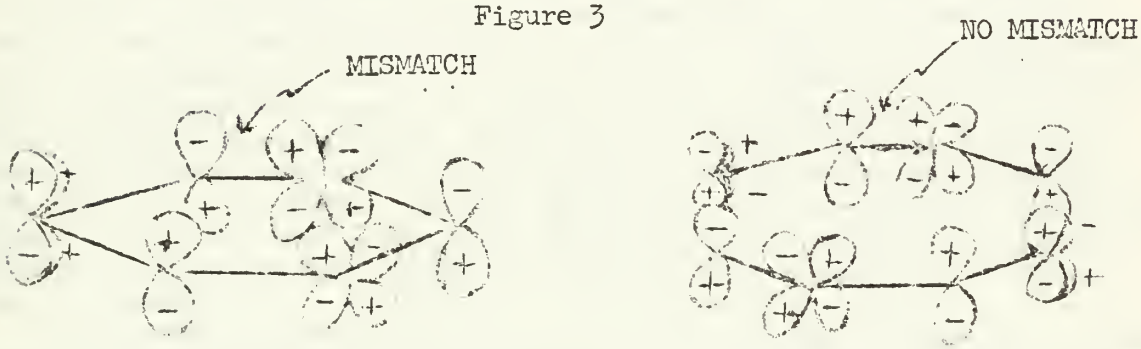


Figure 3



SIX MEMBERED RING

EIGHT MEMBERED RING

In figure 1, the relative energy levels are plotted for the π-electrons of six and eight membered rings for both p_π-p_π and p_π-d_π interactions. Figure 3 is an overlap diagram for the six and eight membered phosphonitrilic rings. In 3a, there is a mismatch in symmetry signs of the participating orbitals, so a particularly stable orbital as found in benzene, consisting of a complete overlap of all atomic orbitals is not possible. However, when there is an even number of both phosphorus and nitrogen atoms, a complete overlap around the ring resulting in a particularly stable orbital is possible. In all cases, any ring consisting of an odd number of phosphorus and nitrogen atoms will have a mismatch and those having an even number will form a stable orbital by a complete overlap of atomic orbitals. This fact is reflected in figure 1. For both the six and eight membered p_π - p_π systems, there is one particularly stable orbital, but it is present only in the eight membered p_π-d_{xz} system.

Other differences are also evident. In the six membered p_π-p_π ring, the highest occupied bonding level is completely filled, leading to a stable system found in benzene. But in the eight membered p_π-p_π ring, the highest occupied level is degenerate and the energy per π-electron is less. However, in the p_π-d_{xz} system, the highest occupied level is non-degenerate in both the six and eight membered rings, leading to increased delocalization energy per π-electron as the ring size increases.

This difference is also reflected in figure 2, where the π-delocalization energy per π-electron is plotted for various ring sizes. The solid line refers to the p_π-p_π system and the broken line to the p_π d_{xz} system. As can be seen, the six membered ring for the p_π-p_π system has greater delocalization energy than that of the eight membered ring. This of course follows from Hückels rule which states that the most stable p_π-p_π systems will be those having $4n + 2$ π electrons. However, there is no comparable rule for p_π-d_π systems since the delocalization energy appears to increase with ring size.

BONDING IN p_π-d_π SYSTEMS:

In order to determine the relative participation of the phosphorus d-orbitals in the bonding of cyclic phosphonitriles, it is useful to look at their orientation as shown in figure 4. Each of the phosphonitriles may be considered a linkage, by nitrogen, of tetrahedral phosphorus atoms, with each phosphorus atom utilizing sp^3 hybrid orbitals for its σ bonds. This hybridization leaves one electron that is promoted to a d-orbital, thereby making it available for π-bonding. The nitrogen utilizes sp^2 hybrids for its σ-bonds. Two sp^2 hybrids are used for bonds to phosphorus atoms and the third is occupied by the lone pair of electrons. The p_z-orbital of nitrogen then contains a single electron which is available for π-bonding.

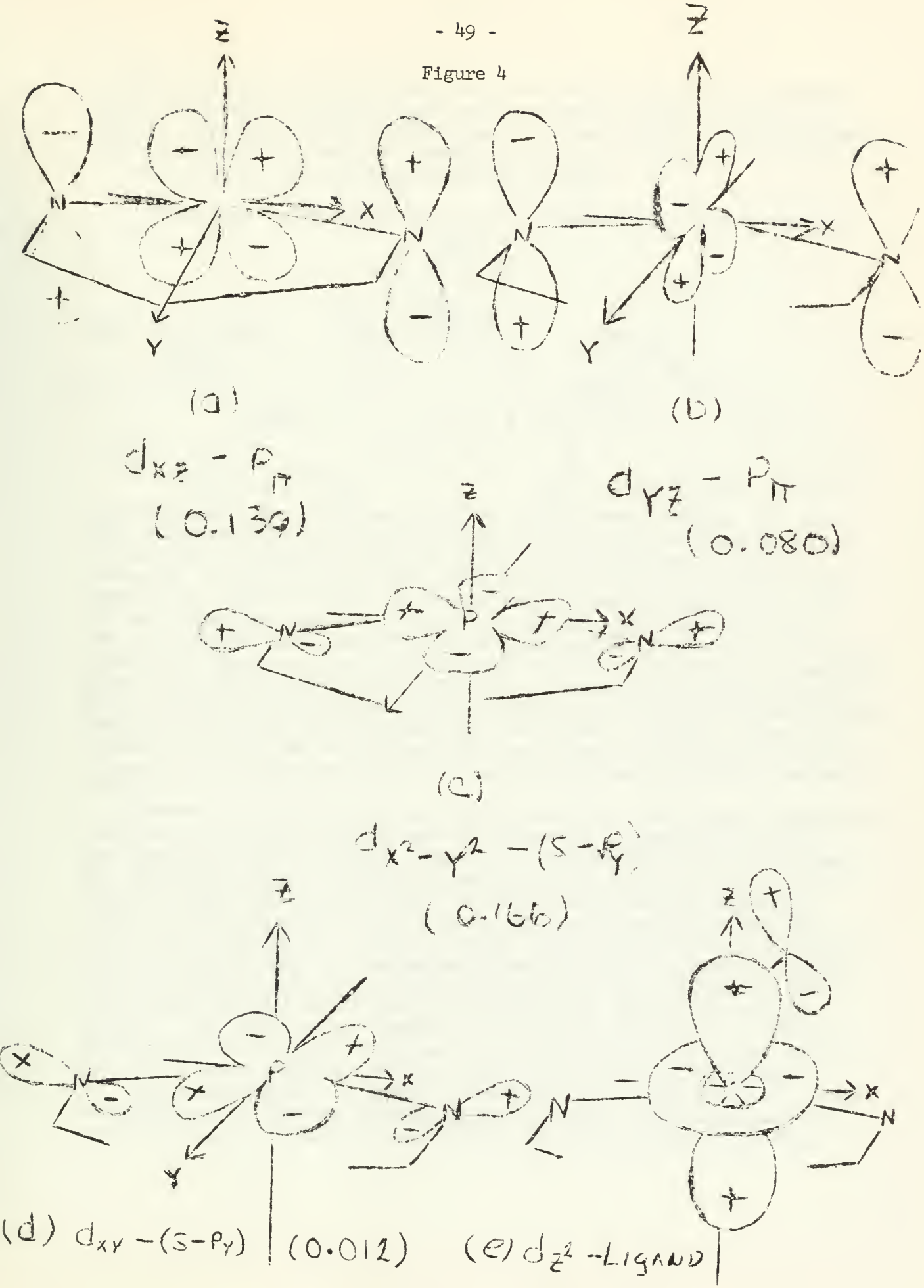
As can be seen, there are two d-orbitals that can overlap the nitrogen p_z-orbital in a planar molecule, namely, the d_{xz} and d_{yz}. Overlap of the nitrogen p_z-orbital with these orbitals is termed the π-system. (9,10,11) The fact that such a π-system can and does form is borne out by results of calculation of overlap integrals, evaluation of heats of formation, and structural determinations. The length and strength of the P-N bond in the phosphonitriles is compared with a P-N single bond in table 1.

Table 1

	$(PNX_2)_3$	Single bond
Length of P-N bond	1.59 A°	1.76 A°
Energy of P-N bond	72.3 kcal.	65 kcal.

Since it is established that the d_{xz} and d_{yz} orbitals of the phosphorus atom can participate in π-bonding with the nitrogen p_z orbital, the next question that arises is whether or not the d_{xz} and d_{yz} orbitals contribute equally, or whether one predominates over the other. If these two orbitals were affected by the electrostatic field created by the surrounding groups in exactly the same manner, then they would be degenerate and contribute equally to the π-bonding. From the values of the overlap integrals of the d_{xz} and d_{yz} orbitals with the nitrogen p_z-orbital in the tetramer (0.139 and 0.080, respectively), there can not be an equal contribution unless some linear combination of the two orbitals were used.

Figure 4


Z
X
Y
N
(a)
$d_{xz} - p_\pi$
(0.139)
(b)
$d_{yz} - p_\pi$
(0.080)
P
(c)
$d_{x^2-y^2} - (s - p_y)$
(0.166)
(d) $d_{xy} - (s - p_y)$
(0.012)
(e) d_{z^2} - LIGAND

Such a linear combination has been postulated by Dewar (15), and the result is a model in which every cyclic P-N bond is equal in length, yet with no π-delocalization. This brings into the picture a model completely different from the classical aromatic delocalized π-systems, since the π-electrons are not continuous around the ring.

The linear combinations used in this argument are shown in figure 5.

Figure 5

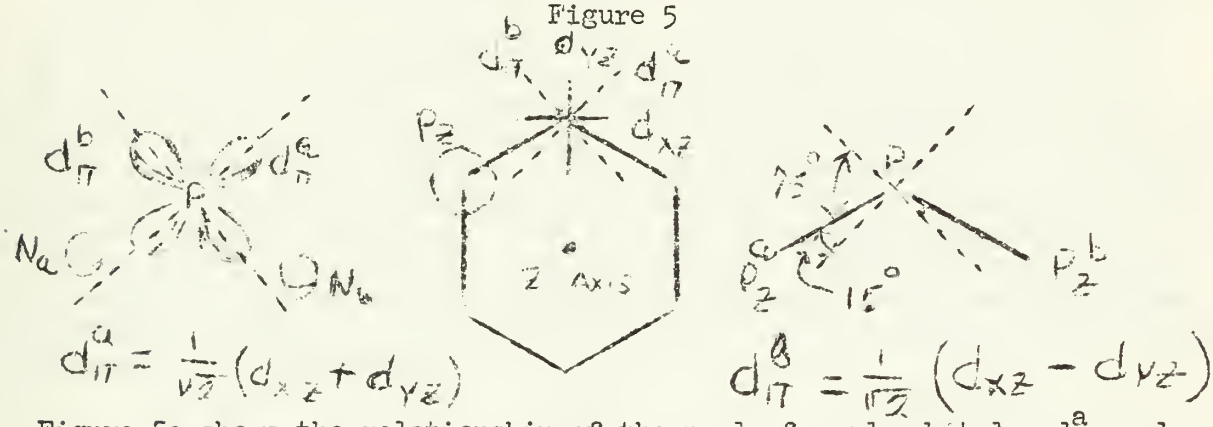


Figure 5a shows the relationship of the newly formed orbitals, d_π^a and d_π^b to the original d_{xz} and d_{yz} orbitals. The newly constructed orbitals lie in planes rotated 45° from the planes of the original d_{xz} and d_{yz} orbitals. As seen in figure 5b, these orbitals will overlap efficiently with the p_z orbital of just one of the two adjacent nitrogen atoms, the d_π^a with nitrogen A and the d_π^b with nitrogen B. The d and p-orbitals are now combined into sets of three centered molecular orbitals as shown in figure 5c. Here one sees an interruption of the π-cloud at each phosphorus atom. Experimental facts were offered by Dewar to substantiate his model. First of all, the short and equal P-N bonds found by an x-ray determination are consistent with the three centered bond model. Secondly, since conjugation is broken at each phosphorus atom, there is no need for planarity of the ring, an important fact since most of the phosphonitriles are not planar.

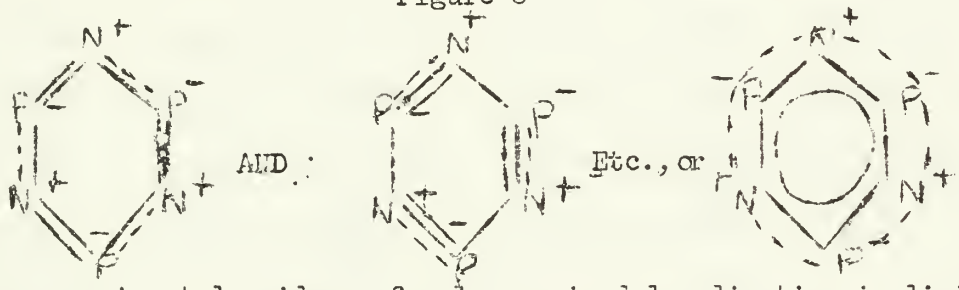
However, the Dewar model is open to question. The primary assumption that the d_{xz} and d_{yz} orbitals have equivalent electronegativities does not seem reasonable. The site symmetry at the phosphorus atom is at most C_{2v}, thereby giving a completely unsymmetrical field relative to the d-orbitals, which will be sufficient to remove all d-orbital degeneracy. Craig has proposed that the d_{xz} orbital will participate more than the d_{yz} in the π system (7). This is based on the fact that the direction of the d-orbitals demands an unequal perturbation by the electron fields of the surrounding atoms. The strong overlap of the d_{yz} orbital with the σ-bonding orbitals would tend to destabilize it relative to the d_{xz} orbital. The fact that the symmetry of the field removes all d-orbital degeneracy does not prove that one or the other of the d_{xz} or d_{yz} orbitals is involved more strongly, but does imply there must be a difference.

The best evidence for unequal participation of these orbitals is found in thermochemical studies of delocalization energy. The Dewar model is not delocalized, therefore, the stability of an individual (PNX_2) unit

should remain constant with increasing ring size. However, the π-delocalization energy per π electron was found to increase with ring size as shown in figure 2. The best conclusion drawn on the basis of available data is that both the d_{xz} and d_{yz} orbitals are involved in the bonding, but the d_{xz}-orbital participates more than the d_{yz}-orbital.

As seen in figures 4c and 4d, the π-system is not the only possible interaction in the ring. There is another possible type of delocalization. The lone pair of electrons on nitrogen are in a hybrid orbital, capable of overlapping the d_{xy} and $d_{x^2-y^2}$ orbitals of phosphorus. Delocalization of the lone pair through this type of bonding scheme would increase the π-character of the ring. The tendency of the phosphorus atom to gain electrons from the nitrogen lone pair increases with the electron withdrawing power of the exocyclic groups. Again there is a controversy as to which of these two orbitals predominates in the bonding, but on the basis of overlap data and symmetry arguments, there will not be an equal participation. The overlap of the d_{xy} and $d_{x^2-y^2}$ orbitals with the nitrogen lone pair orbital is designated the π' system. A schematic drawing of the π and π' systems is shown in figure 6. As is seen, both the π and π' systems tend to increase the amount of delocalization.

Figure 6



The experimental evidence for lone pair delocalization is limited, but there is some indication that delocalization exists. Inconclusive evidence has been reported from the results of infrared studies(16-21) and the base strength of the derivatives (22,23).

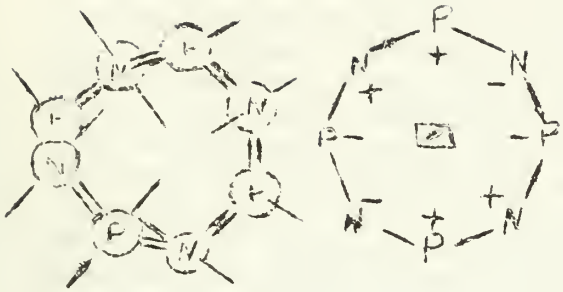
MOLECULAR CONFIGURATIONS:

Thus far, nothing has been said about the relative amounts of π and π' character. A study of molecular configurations helps to evaluate this as well as give further evidence for the existence of the π and π' systems. As the ring size is increased, the structures will necessarily deviate from planarity because of the strain in the large P-N-P angles that would otherwise result. But the various configurations that are adopted cannot be explained only in terms of steric effects, and the fact that the tetrameric fluoride is planar with a P-N-P angle of 147° implies that there is something more involved than simply finding a stable configuration on a steric basis.

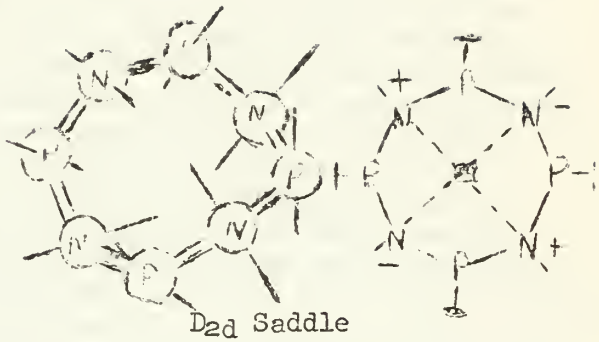
The possible configurations for tetrameric derivatives are found in figure 7. The values for overlap integrals for the various interactions are listed beneath each configuration.

In order to predict what configuration a particular derivative will adopt, we must first include π and π' bonding and secondly, steric inter-

Figure 7



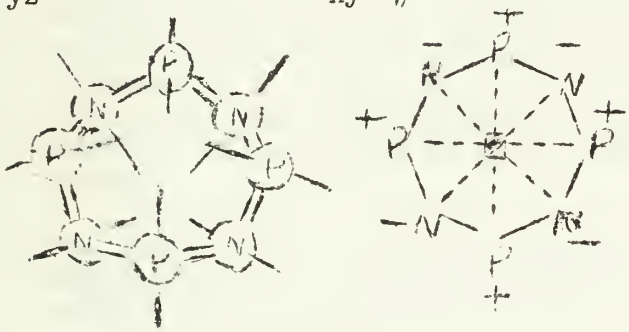
S_4 Tub



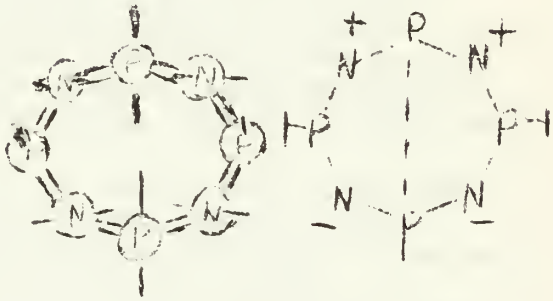
D_{2d} Saddle

OVERLAP INTEGRALS

d_{xz}-p_{π} = 0.109	$d_{x^2-y^2}$ - sp = 0.147	d_{xz}-p_{π} = 0.133	$d_{x^2-y^2}$ -sp = 0.150
d_{yz}-p_{π} = 0.063	d_{xy}-sp = 0.042	d_{yz}-p_{π} = 0.065	d_{xy}-sp = 0.040
d_{xz}-sp = 0.058	$d_{x^2-y^2}$ - p_{π} = 0.069	d_{xz}-sp = 0.068	$d_{x^2-y^2}$-p_{π} = 0.081
d_{yz}-sp = 0.033	d_{xy}-p_{π} = 0.040	d_{yz}-sp = 0.039	d_{xy}-p_{π} = 0.047



C_{4v} Crown



C_2 Chair

OVERLAP INTEGRALS

d_{xz}-p_{π} = 0.068	$d_{x^2-y^2}$-sp = 0.112	d_{xz}-p_{π} = 0.080	$d_{x^2-y^2}$-sp = 0.123
d_{yz}-p_{π} = 0.039	d_{xy}-sp = 0.062	d_{yz}-p_{π} = 0.046	d_{xy}-sp = 0.056
d_{xz}-sp = 0.102	$d_{x^2-y^2}$-p_{π} = 0.122	d_{xz}-sp = 0.082	$d_{x^2-y^2}$-p_{π} = 0.097
d_{yz}-sp = 0.059	d_{xy}-p_{π} = 0.070	d_{yz}-sp = 0.047	d_{xy}-p_{π} = 0.056

actions. In the tub and chair configurations, the steric interactions are at a minimum since the neighboring PX_2 groups are staggered, while in the crown and saddle forms, steric interactions are high since the PX_2 groups are in the eclipsed position. The configurations that favor π and π' bonding can be found from the values of overlap integrals. The values listed for the tub and chair configurations are averages over all overlaps of the named types, for instance, the individual values for the p_π-d_{xz} overlap in the tub are .080 and .137. The magnitude of overlap for p_π-d_π bonding is largest in the tub and saddle configurations and lowest in the chair and crown. Since the d_π and $d_{\pi'}$ orbitals are mutually perpendicular, p_π-$d_{\pi'}$ interactions will be weak when the p_π-d_π are strong. This is also reflected in the values of the overlap integrals. The π' interactions involving the d_{xy} and $d_{x^2-y^2}$ orbitals of phosphorus and the lone-pair hybrid orbital of the nitrogen are strong in all cases, being particularly favorable in the tub and saddle forms. Since the crown form combines the highest steric repulsions with the weakest π bonds, it is likely that no phosphonitrile will have this structure.

The values of the overlap integrals for the S_4 tub structure indicate that the d_{xz} and d_{yz} orbitals do take part in π bonds and both the $d_{x^2-y^2}$ and d_{xy} orbitals in π' bonds. However, delocalization is prevented in the π system since only the p_π-d_{xz} interactions between nitrogen and phosphorus atoms on the same side of the molecular plane are strong. But there are still other possibilities. The overlap values indicate a good overlap between the nitrogen p_π-orbital and the phosphorus $d_{\pi'}$ orbitals, the $d_{x^2-y^2}$ and the d_{xy} orbitals. A combination of this interaction with the interaction of the nitrogen p_π and phosphorus d_π orbitals will give a structure in which the phosphorus d_{xz} orbital overlaps one nitrogen p_π orbital and the phosphorus d_{xy} and $d_{x^2-y^2}$ orbitals overlap the p_π orbital of the other neighboring nitrogen. The p_π-orbital on this nitrogen then interacts with the next phosphorus d_{xz} orbital adjacent to it. There is still no conjugation since the d_{xz} and d_{xy} are not degenerate in the symmetry of the field. Instead, there are three-centered bonds similar to those postulated by Dewar, leading to equal bond lengths.

The remaining D_{2d} saddle configuration has larger steric repulsions, but p_π-d_{xz} orbital overlap results in a delocalized system. This is necessarily true because the dihedral angles between successive z-axes are equal, thereby equalizing p_π-d_{xz} interactions around the ring.

Since there is no configuration that gives both minimized repulsions and strong π-bonding, it is expected that the configurations found for the tetrameric derivatives will show some compromise between the saddle and tub configurations. The crystal structures of four tetramers are known, and indeed there is a compromise shown between these two configurations. The only reason that the tub configuration can't have a strong π system is because of the energy difference between the π and π' orbitals. If the d_{xz} and d_{xy} orbitals were of equal energy and equal overlapping ability, a delocalized system could result using these two orbitals. But the symmetry of the field on the phosphorus atom predicts that the d_{xy} orbital will be of higher energy. But the d_{xy} orbital is a π' orbital, and therefore tends to gain electron density from the lone pair orbital, thereby stabilizing it. As lone pair delocalization increases, the π' orbitals

approach the π orbitals in energy. When this happens, the π' orbitals approach the π orbitals in their overlapping ability with the nitrogen p_π orbital, and a strong π system can result even in the tub structure. Thus the real configuration observed should be an accurate way of measuring the relative amount of π and π' bonding in the ring.

Table 4 gives the displacements of the ring atoms from the mean molecular plane for three non-planar tetrameric molecules. The ratio decreases as symmetry D_{2d} is approached, and would be zero for perfect D_{2d} symmetry.

Table 4

$(NPX_2)_4$	$(NPCl_2)_4$	$(NPMe_2)_4$	$[NP(NMe_2)_2]_4$
Displacements of P	0.35	0.21	0.18
Displacements of N	0.47	0.54	0.52
Ratio P/N	0.75	0.39	0.35

The exocyclic groups release electrons to the phosphorus decreasing in the order $Me_2N > CH_3 > Cl$. In the tetrameric dimethylamide, electronic feedback tends to prevent delocalization of the lone pairs on the nitrogen atoms so that the π' bonding is weak and the resulting configuration is closest to the saddle, D_{2d}. Electron release is less from methyl and least from chlorine, so that π' bonding increases and the configuration, now controlled more by steric interactions, departs increasingly from the D_{2d} symmetry towards the S_4 structure in which the phosphorus and nitrogen atoms are displaced equally from the ring.

The tetrameric fluoride on the other hand was found to be planar by an x-ray determination. (25) This would appear at first glance to be a highly strained system, since the P-N-P ring angle is 147°. However, the high electronegativity of the fluorine will increase lone pair delocalization, and does so to such an extent that the nitrogen ring bonds can be displaced into the region formerly occupied by the lone pair, giving the resultant 147° angle.

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ABSTRACT

CATIONS OF IODINE

R. Fitzgerald November 9, 1965

Introduction

Iodine, being the most electropositive of the common halogens should be the halogen most likely to form cations. The early discovery that iodine and iodine monochloride form conducting solutions in ethanol[1], led to what Arotsky and Symons[2] have termed "an almost obsessive desire to prove the existence and comparative stability of iodine cations in chemical systems". As a result iodine cations have often been proposed in systems where their existence is chemically improbable.[1,3,4]

Enthusiasm for I^+ in aqueous solutions has been curbed by a paper concerned with the thermodynamic aspects of formation of halogen cations in solution.[5] From this work it appears unlikely I^+ could exist as anything except a transient intermediate in aqueous solutions.

Since iodine has a tendency to form covalently bonded compounds, in which it formally exists in a positive oxidation state, positively-charged iodine compounds where the iodine appears at the cathode in electrolysis are quite common.[2] Perhaps as a result, there remains much confusion in the literature over the terms "positive iodine" and "iodine cations" and there have appeared works[6,7,8] which purport to deal with halogen cations, but in fact are vague in differentiating between cations and positive halogen compounds. In this seminar iodine cations will refer to the simple cationic species in solution. The vast majority of previous work has dealt with cationic iodine in compounds or complexes. Several excellent texts and reviews on this subject and its chemistry are available.[9,10,11,12] Iodine cations have also been proposed as transient intermediates in reactions of iodine compounds in aqueous systems.[33]

Recently the existence and properties of iodine cations in solution have been extensively investigated. This seminar will be concerned with that aspect of the subject and limited to the ions I^+, I_3^+, and I_5^+.

Chemical Properties

I^+ It has been known for many years that I^+ (g) exists when iodine vapor is decomposed by an electric arc.[13,14] From Murakawa's results it is possible to show that as expected I^+ (g) shows a $5S^2P^4$ and $^3P_2$ ground state. Past attempts to study the free cation have utilized detection of its unit positive charge and high electrophilic powers. The results[15] have often been ambiguous at best. However, two other properties offer much more promise for the detection of iodine cations. Due to two unpaired electrons in its outer shell, the iodine cation would be expected to be paramagnetic in its ground state.[15] At first glance, the visible spectrum does not seem promising since calculations for iodine in the gas phase[14] showed no allowed transition above 200mμ. However, later experimental work has shown at least one characteristic band for I^+ in the visible region. This problem will be discussed in more detail later.

In general iodine cations may be expected to exist only in weakly nucleophilic solvents which also possess high ionizing power.[2] An additional requirement is that there be no reducing agent present capable of reducing the cations to iodine. When I^+ is the cation in question, there should also be no strong oxidizing agent present. Sulfuric acid has proved to be a convenient solvent and more recently fluorosulfuric acid[16] and iodine pentafluoride[17] have been used successfully.

I_3^+ As Mason first pointed out I_3^+ should be more stable than I^+ on the basis of its electronic configuration.[18] Walsh has predicted a bent structure[19] and recent studies[20,21] on a number of compounds containing the isoelectronic ion ICl_2^+ have shown angle of $\sim 90°$. Symons[22] has also pointed out that by analogy with Cl_2O, I_3^+ should be bent, diamagnetic, and possess low-lying electronic transitions. It is significant that this ion has a unit positive charge and is a powerful electrophilic iodinating agent, thus offering possible confusion with I^+.[2]

I_5^+ Only one definitive claim for this ion has been made[23], but others have speculated as to its presence[18,24], and Symons has suggested a cyclic structure for it.[24] Like I^+ and I_3^+, I_5^+ also appears to be a powerful iodinating agent.[18]

Previous Research

A compilation of previous work is found in Table 1.

Interpretations of Magnetic and Spectral Properties

Two results need further clarification, the unexpectedly low magnetic moments found for I^+ and nature of the splitting in the spectra.

Symons' first measurements[15] showed unexpectedly low moments, since a "spin-only" value would equal 2.83 B.M. The results for this and other measurements are given in Table 2.

Disatisfied with their first measurements, Symons, et.al. redid the moments by N.M.R.[27] At this time they also failed to detect any E.S.R. signal. Other moments done later[26] and in different solvents[17] give substantially the same results. Arotsky and Symons suggested a possible answer to the problem[26] and adapting a theory developed by Katani[28], they calculated a moment of 1-4 B.M. Later Arotsky and Symons[2] suggested that the moment may be lowered due to the coupling of excited singlet states splitting the $^3\Sigma$ ground state.

Pasternak and Piper[29] attempted a more sophisticated treatment of the data. On the basis of a crystal field calculation, assuming the approach of a negative ligand on the Z axis, they proposed that the low moment was due to a nearly equal population of the $^1\Sigma$ and $^3\pi$ states. Although their calculations are correct, their treatment is essentially irrelevant to the magnetic problem, since the problem is actually comparable to a positive axial field.[30,17] In a later note[30] Arotsky and Symons concluded that preferential solvation in the xy plane leading to a $^3\Sigma$ ground state, although crude, still fit the data best.

It should be noted that all moments were calculated assuming I^+ was formed quantitatively. Support for this was furnished by Symons' et.al.

rather dubious claim[26,31] that conductometric studies and conductometric titrations showed are positive charge per iodine atom. However, Gillespie et.al.[23] later estimated by means of cryoscopy and conductivity studies that at a mole ratio of (I_2/HIO_3 = 2.0) only 1/3 of the iodine was present as I^+. Symons has changed his mind three times[22,26,24] on whether I_3^+ is simultaneously present with I^+—at last report he believed it was.

If one notes the trend of increasing moment with decreasing concentration together with Gillespie's work, it seems most likely that simultaneous equilibria are set up, with low concentrations of iodine favoring I^+ [23], thus accounting for the low magnetic moment. Although Symons suggested in his first paper[15] that temperature dependence studies be done, no work has been reported on this. Together with further E.S.R. work this should bring considerable insight to the problem.

Although calculations by Murakawa[14] showed no allowed transitions for I^+ (g) above 200 mμ. Later experimental work has shown three characteristic bands for I^+, as well as bands for I_3^+ and I_5^+, in the u v and visible regions. The first attempt at the assignment of transitions in I^+ was made by Symons.[22] Later Symons, et.al.[26] applied a "crystal field" approach and proposed that there would be "preferrential solvation," in the xy plane, due to the unfilled p orbitals. They deduced the levels would be split into a $^3\Sigma$ ground state and low-lying $^3\pi_i$ states (i = 0,1,2). Using earlier calculations[32], they assigned the transitions $^3\Sigma \rightarrow {}^3\pi_2$, which they correctly predicted should be most intence, $^3\Sigma \rightarrow {}^3\pi_1$ and $^3\Sigma \rightarrow {}^3\pi_0$ although these transitions remain formally forbidden, Symons et.al.[2] have noted that second- and third-- row transition-metal complexes often show large deviations from this, and explained the intensities by "higher-state mixing" with the 5d orbitals and "borrowing" intensity from charge-transfer transitons involving orientated solvent molecules. In their paper Pastermak and Piper[30] also attempted to explain the observed spectra and assigned the transitions to $^1\pi$, $^3\Sigma$, and $^1\Delta$ respectively. They concluded that the crystal field model did not accurately fit the spectra. It is more interesting to note that if one uses the proper crystal field, the numerical fit is still poor. This suggest s that Symons' et. al. assignment are not definite and that further work is needed.

Table 1

Solvent	Source of Iodine	Oxidant	Species	References
H_2SO_4	I_2	Hg_2SO_4, $HgSO_4$ IO_3^-, IO_4^-, MnO_2, MnO_4^-	I^+	25
H_2SO_4	I_2	$(IO)_2SO_4$	I^+, I_3^+, I_5^+	18
65% oleum	I_2	SO_3	I^+	15
30% oleum	I_2	---	I_3^+	22
65% oleum	ICl	---	I^+	26
H_2SO_4 dil oleum	I_2	HIO_3 (1:1) I_2O_5 (1:1) $(IO)_2SO_4$	I_3^+	24
H_2SO_4	I_2	---	I_5^+	24
IF_5	I_2	H_2O	I^+	17
IF_5	ICl	H_2O	I^+	17
HSO_3F	$IOSO_2F$	---	I^+	16
HSO_3F	I_3OSO_2F	---	I_3^+	16
H_2SO_4	I_2	HIO_3 (2:1)	I^+	23
H_2SO_4	I_2	HIO_3 (7:1)	I_3^+	23
H_2SO_4	I_2	HIO_3 (> 7:1)	I_5	23

Table 2

μ Ave. (B.M.)	Conc. of I^+	Solvent	References
1.90 ± .1	.1 M	Conc. oleum	15
2.50 ± .4	.01 M	Conc. oleum	15
1.5	.401 M	Conc. oleum	27
1.44	(.1-1.0 M)	Conc. oleum	26
1.54	(.1-1.0 M)	Conc. oleum	26
∿ 2	.0716 M	IF_5	17

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Introduction

Iodine, being the most electropositive of the common halogens should be the halogen most likely to form cations. The early discovery that iodine and iodine monochloride form conducting solutions in ethanol[1], led to what Arotsky and Symons[2] have termed "an almost obsessive desire to prove the existence and comparative stability of iodine cations in chemical systems". As a result iodine cations have often been proposed in systems where their existence is chemically improbable.[1,3,4]

Enthusiasm for I^+ in aqueous solutions has been curbed by a paper concerned with the thermodynamic aspects of formation of halogen cations in solution.[5] From this work it appears unlikely I^+ could exist as anything except a transient intermediate in aqueous solutions.

Since iodine has a tendency to form covalently bonded compounds, in which it formally exists in a positive oxidation state, positively-charged iodine compounds where the iodine appears at the cathode in electrolysis are quite common.[2] Perhaps as a result, there remains much confusion in the literature over the terms "positive iodine" and "iodine cations" and there have appeared works[6,7,8] which purport to deal with halogen cations, but in fact are vague in differentiating between cations and positive halogen compounds. In this seminar iodine cations will refer to the simple cationic species in solution. The vast majority of previous work has dealt with cationic iodine in compounds or complexes. Several excellent texts and reviews on this subject and its chemistry are available.[9,10,11,12] Iodine cations have also been proposed as transient intermediates in reactions of iodine compounds in aqueous systems.[33]

Recently the existence and properties of iodine cations in solution have been extensively investigated. This seminar will be concerned with that aspect of the subject and limited to the ions I^+, I_3^+, and I_5^+.

Chemical Properties

I^+ It has been known for many years that I^+ (g) exists when iodine vapor is decomposed by an electric arc.[13,14] From Murakawa's results it is possible to show that as expected I^+ (g) shows a $5S^2P^4$ and $^3P_2$ ground state. Past attempts to study the free cation have utilized detection of its unit positive charge and high electrophilic powers. The results[15] have often been ambiguous at best. However, two other properties offer much more promise for the detection of iodine cations. Due to two unpaired electrons in its outer shell, the iodine cation would be expected to be paramagnetic in its ground state.[15] At first glance, the visible spectrum does not seem promising since calculations for iodine in the gas phase[14] showed no allowed transition above 200mμ. However, later experimental work has shown at least one characteristic band for I^+ in the visible region. This problem will be discussed in more detail later.

In general iodine cations may be expected to exist only in weakly nucleophilic solvents which also possess high ionizing power.[2] An additional requirement is that there be no reducing agent present capable of reducing the cations to iodine. When I^+ is the cation in question, there should also be no strong oxidizing agent present. Sulfuric acid has proved to be a convenient solvent and more recently fluorosulfuric acid[13] and iodine pentafluoride[17] have been used successfully.

I_3^+ As Mason first pointed out I_3^+ should be more stable than I^+ on the basis of its electronic configuration.[18] Walsh has predicted a bent structure[19] and recent studies[20,21] on a number of compounds containing the isoelectronic ion ICl_2^+ have shown angle of $\sim 90°$. Symons[22] has also pointed out that by analogy with Cl_2O, I_3^+ should be bent, diamagnetic, and possess low-lying electronic transitions. It is significant that this ion has a unit positive charge and is a powerful electrophilic iodinating agent, thus offering possible confusion with I^+.[2]

I_5^+ Only one definitive claim for this ion has been made[23], but others have speculated as to its presence[19,24], and Symons has suggested a cyclic structure for it.[24] Like I^+ and I_3^+, I_5^+ also appears to be a powerful iodinating agent.[18]

Previous Research

A compilation of previous work is found in Table 1.

Interpretations of Magnetic and Spectral Properties

Two results need further clarification, the unexpectedly low magnetic moments found for I^+ and nature of the splitting in the spectra.

Symons' first measurements[15] showed unexpectedly low moments, since a "spin-only" value would equal 2.83 B.M. The results for this and other measurements are given in Table 2.

Disatisfied with their first measurements, Symons, et.al. redid the moments by N.M.R.[27] At this time they also failed to detect any E.S.R. signal. Other moments done later[26] and in different solvents[17] give substantially the same results. Arotsky and Symons suggested a possible answer to the problem[26] and adapting a theory developed by Katani[28], they calculated a moment of 1-4 B.M. Later Arotsky and Symons[2] suggested that the moment may be lowered due to the coupling of excited singlet states splitting the $^3\Sigma$ ground state.

Pasternak and Piper[29] attempted a more sophisticated treatment of the data. On the basis of a crystal field calculation, assuming the approach of a negative ligand on the Z axis, they proposed that the low moment was due to a nearly equal population of the $^1\Sigma$ and $^3\pi$ states. Although their calculations are correct, their treatment is essentially irrelevant to the magnetic problem, since the problem is actually comparable to a positive axial field.[30,17] In a later note[30] Arotsky and Symons concluded that preferential solvation in the xy plane leading to a $^3\Sigma$ ground state, although crude, still fit the data best.

It should be noted that all moments were calculated assuming I^+ was formed quantitatively. Support for this was furnished by Symons' et.al.

rather dubious claim[26,31] that conductometric studies and conductometric titrations showed are positive charge per iodine atom. However, Gillespie et.al.[23] later estimated by means of cryoscopy and conductivity studies that at a mole ratio of (I_2/HIO_3 = 2.0) only 1/3 of the iodine was present as I^+. Symons has changed his mind three times[22,26,24] on whether I_3^+ is simultaneously present with I^+—at last report he believed it was.

If one notes the trend of increasing moment with decreasing concentration together with Gillespie's work, it seems most likely that simultaneous equilibria are set up, with low concentrations of iodine favoring I^+ [23], thus accounting for the low magnetic moment. Although Symons suggested in his first paper[15] that temperature dependence studies be done, no work has been reported on this. Together with further E.S.R. work this should bring considerable insight to the problem.

Although calculations by Murakawa[14] showed no allowed transitions for I^+ (g) above 200 mμ. Later experimental work has shown three characteristic bands for I^+, as well as bands for I_3^+ and I_5^+, in the u v and visible regions. The first attempt at the assignment of transitions in I^+ was made by Symons.[22] Later Symons, et.al.[26] applied a "crystal field" approach and proposed that there would be "preferrential solvation," in the xy plane, due to the unfilled p orbitals. They deduced the levels would be split into a $^3\Sigma$ ground state and low-lying $^3\pi_i$ states (i = 0,1,2). Using earlier calculations[32], they assigned the transitions $^3\Sigma \rightarrow {}^3\pi_2$, which they correctly predicted should be most intence, $^3\Sigma \rightarrow {}^3\pi_1$ and $^3\Sigma \rightarrow {}^3\pi_0$ although these transitions remain formally forbidden, Symons et.al.[2] have noted that second- and third-row transition-metal complexes often show large deviations from this, and explained the intensities by "higher-state mixing" with the 5d orbitals and "borrowing" intensity from charge-transfer transitons involving orientated solvent molecules. In their paper Pastermak and Piper[30] also attempted to explain the observed spectra and assigned the transitions to $^1\pi$, $^3\Sigma$, and $^1\Delta$ respectively. They concluded that the crystal field model did not accurately fit the spectra. It is more interesting to note that if one uses the proper crystal field, the numerical fit is still poor. This suggests that Symons' et. al. assignment are not definite and that further work is needed.

Table 1

Solvent	Source of Iodine	Oxidant	Species	References
H_2SO_4	I_2	Hg_2SO_4, $HgSO_4$ IO_3^-, IO_4^-, MnO_2, MnO_4^-	I^+	25
H_2SO_4	I_2	$(IO)_2SO_4$	I^+, I_3^+, I_5^+	18
65% oleum	I_2	SO_3	I^+	15
30% oleum	I_2	---	I_3^+	22
65% oleum	ICl	---	I^+	26
H_2SO_4 dil oleum	I_2	HIO_3 (1:1) I_2O_5 (1:1) $(IO)_2SO_4$	I_3^+	24
H_2SO_4	I_2	---	I_5^+	24
IF_5	I_2	H_2O	I^+	17
IF_5	ICl	H_2O	I^+	17
HSO_3F	$IOSO_2F$	---	I^+	16
HSO_3F	I_3OSO_2F	---	I_3^+	16
H_2SO_4	I_2	HIO_3 (2:1)	I^+	23
H_2SO_4	I_2	HIO_3 (7:1)	I_3^+	23
H_2SO_4	I_2	HIO_3 (> 7:1)	I_5	23

Table 2

μ Ave. (B.M.)	Conc. of I^+	Solvent	References
1.90 ± .1	.1 M	Conc. oleum	15
2.50 ± .4	.01 M	Conc. oleum	15
1.5	.401 M	Conc. oleum	27
1.44	(.1-1.0 M)	Conc. oleum	26
1.54	(.1-1.0 M)	Conc. oleum	26
∿ 2	.0716 M	IF_5	17

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NMR LINEWIDTH STUDIES OF LIGAND EXCHANGE REACTIONS OF TRANSITION METAL COMPLEXES

Steven S. Zumdahl November 16, 1965

Introduction:

In the past several years, n.m.r. has become a significant tool in the study of a great variety of fast chemical reactions. One application of this type which is of special interest to inorganic chemists is the study of ligand exchange reactions of transition metal complexes. Much of the work in this area has involved study of the n.m.r. linewidth as a means to obtain the exchange rate constant.

Theory

Many applications of n.m.r., including kinetic studies, are based on the Bloch equations,[1,2,3] which describe the variation of the resultant macroscopic magnetic moment $\vec{M}$ ($\vec{M}_x$, $\vec{M}_y$, $\vec{M}_z$) for an assembly of identical magnetic nuclei. The variation in $\vec{M}$ can be attributed to three main sources: (1) the steady field H_o, (2) the oscillating r.f. field H_1, and (3) relaxation processes. Since $\frac{d\vec{M}}{dt} = \gamma (\vec{M} \times \vec{H})$, where γ is the magnetogyric ratio of the nuclei concerned, equations can be written for the variation of the components of $\vec{M}$ due to the above three sources. After transformation to a set of perpendicular axes u and v rotating in the xy plane with angular velocity $-\omega$, these equations are:

$$(1) \quad \frac{du}{dt} + \frac{u}{T_2} + (\omega_o - \omega)v = 0$$

$$(2) \quad \frac{dv}{dt} + \frac{v}{T_2} - (\omega_o - \omega)u + \gamma H_1 M_z = 0$$

$$(3) \quad \frac{dM_z}{dt} + \frac{M_z - M_o}{T_1} - \gamma H_1 v = 0$$

where $\omega_o = \gamma H_o$, M_o is the equilibrium value of M, and T_1 and T_2 are the longitudinal and transverse relaxation times respectively.

In a system where more than one type of magnetic nuclei is present, the Bloch equations must be modified. This was first done by Gutowsky et.al.[4] and later by McConnell[5] who treated the problem as follows:

A total transverse moment, G = u + iv, is defined for each magnetic site. Thus, from (1) and (2) an equation can be obtained for the $_j$th magnetic site in terms of G_j:

$$(4) \quad \frac{dG_j}{dt} + \left[\frac{1}{T_{2j}} - i\,(\omega_j - \omega)\right] G_j = -i\,\gamma H_1 M_{oj}$$

Consider a system with two sites, A and B, in which exchange of magnetic nuclei is occurring. Equation (4) must be modified to account for magnetic nuclei moving into and out of a given site. This gives for site A:

$$(5)\quad \frac{dG_A}{dt} + \left[\frac{1}{T_{2A}} - i\,(\omega_A - \omega)\right] G_A = -i\,\gamma\, H_1\, M_{oA} + \frac{G_B}{\tau_B} - \frac{G_A}{\tau_A}$$

where τ_A and τ_B are the mean lifetimes of a magnetic nucleus at site A and site B respectively. Thus, G_B/τ_B represents the rate of increase of G_A due to transfer of nuclei from B to A, and $-G_A/\tau_A$ represents the loss of G_A due to transfer of nuclei from A to B. An analogous equation can be written for site B.

Assuming slow passage conditions ($\frac{dG_A}{dt} = \frac{dG_B}{dt} = 0$), these equations can be solved for G_A and G_B. The total transverse magnetic moment for the system is $G = G_A + G_B$. Since the absorption experiment in n.m.r. is set up so that the intensity of the observed signal only depends upon v, a line-shape function $g(\nu)$ can be obtained by solving for the imaginary part of G. Then from the lineshape function it can be shown that the width of the signal at half maximum intensity ($\Delta\omega$) is equal to $2/T_2$.

For application to chemical systems consider the following limiting cases:

1. Slow Exchange - When τ_A and τ_B are sufficiently large, two peaks are observed. When $\omega \cong \omega_A$, $G \cong G_A$, and $G_B \cong 0$. When $\omega \cong \omega_B$, $G \cong G_B$, and $G_A \cong 0$. Thus the lineshape functions for peaks A and B are gotten from G_A and G_B separately. From the lineshape function for A it is found that [15]

$$(6)\quad 2/T_{2A}' = \Delta\omega \quad \text{(radians/sec)}$$

where

$$(7)\quad \frac{1}{T_{2A}'} = \frac{1}{T_{2A}} + \frac{1}{\tau_A} = \pi\,\Delta\nu \quad \text{(cps)}$$

and similarly for peak B.

2. Intermediate exchange in dilute solution of complex--Swift and Connick[6] using McConnell's method derived a lineshape function for a system consisting of a dilute solution of a metal complex in the presence of excess ligand (i.e. $P_A >> P_M$ where P_M and P_A represent the mole fractions of coordinated ligand and bulk ligand respectively). From the lineshape function an expression is obtained for the linewidth of the observed signal

$$(8)\quad \frac{\Delta\omega}{2} = \frac{1}{T_2} = \frac{1}{T_{2A}} + \frac{1}{\tau_A}\left[\frac{\frac{1}{T_{2M}^2} + \frac{1}{T_{2M}\tau_M} + \Delta\omega_M^2}{\left(\frac{1}{T_{2M}} + \frac{1}{\tau_M}\right)^2 + \Delta\omega_M^2}\right]$$

where M and A represent the coordinated and free ligand sites respectively and $\Delta\omega_M = \omega_M - \omega_A$.

Relaxation Effects of Paramagnetic Ions

Paramagnetic species in solution greatly enhance both transverse and longitudinal relaxation processes. This can be explained in terms of two relaxation mechanisms:

(1) The dipolar mechanism formulated by Solomon[7], which results from nuclear spin-electron spin dipole-dipole interactions, has a correlation time τ_c defined by the expression:

$$\frac{1}{\tau_c} = \frac{1}{\tau_s} + \frac{1}{\tau_r}$$

where τ_s is the lifetime of the electron spin state
τ_r is the correlation time for the tumbling of the paramagnetic ion.

(2) The exchange mechanism suggested by Bloembergen[8], which results from nuclear spin-electron spin scalar coupling, has a correlation time τ_e where

$$\frac{1}{\tau_e} = \frac{1}{\tau_s} + \frac{1}{\tau_M}$$

where τ_M is the mean lifetime of a ligand in the first coordination sphere of the metal.

Since transition probabilities are additive,

$$\frac{1}{T} = \left(\frac{1}{T}\right)_{dipolar} + \left(\frac{1}{T}\right)_{exchange} \qquad \text{where } T = T_1 \text{ and } T_2$$

Thus, combining the results of Solomon and Bloembergen:

$$(9) \quad \frac{1}{T_{1M}} = K_1 \left[3\tau_c + \frac{7\tau_c}{1+\omega_s^2\tau_c^2}\right] + K_2 \left[\frac{\tau_e}{1+\omega_s^2\tau_e^2}\right]$$

$$(10) \quad \frac{1}{T_{2M}} = \frac{K_1}{2} \left[7\tau_c + \frac{13\tau_c}{1+\omega_s^2\tau_c^2}\right] + \frac{K_2}{2} \left[\tau_e + \frac{\tau_e}{1+\omega_s^2\tau_e^2}\right]$$

where K_1 and K_2 are constants and ω_s is the Larmor frequency for the electron spin moment.

Consider the limiting cases:

1. If $\omega_s^2\tau_e^2 << 1$ (i.e., τ_s is small), $T_1 = T_2$

2. If $\omega_s^2\tau_e^2 >> 1$ (i.e., τ_s is large), $T_1 > T_2$

(See references 9 and 10 for a more complete treatment.)

An additional mechanism appearing in equation (8) is the "so called" contact shift mechanism[11] represented by $\Delta\omega_M$. This mechanism enhances relaxation by a change in the precessional frequency between sites A and M.

Temperature Dependencies of the Relaxation Mechanisms

The temperature dependencies of the relaxation processes can be used to distinguish line broadening due to exchange from that due to relaxation.

Processes with exponential temperature dependence obey an expression of the type

$$(11) \quad \tau_j = \tau_j^{o} \; e^{V_j/RT}$$

where V_j is the activation energy and $\tau_j = \tau_M$ and τ_r. The temperature dependence of τ_s can be obtained from the expression by Bloembergen and Morgan[10]

$$(12) \quad \frac{1}{\tau_s} = K_3 \frac{\tau_v}{1+\omega_s^2\tau_v^2} + K_4 \frac{\tau_v}{1+\omega_s^2\tau_v^2}$$

where τ_v is the correlation time for the collision of solvent molecules with the solvated ion. τ_v obeys (11) also.

The temperature dependence of $\Delta\omega_M$ is given by the contact shift equation[8].

$$(13) \quad \frac{\Delta\omega_M}{\omega} = \frac{K_5}{T}$$

Applications

A. Exchange Rates of Aquo Complexes Using O^{17} Resonance

Swift and Connick[6] studied the exchange rates of the aquo complexes of Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2} and Cu^{+2} by observation of the O^{17} signal due to the weighted average of coordinated and free water molecules. Exchange rates were obtained from equation (8) by consideration of the following limiting cases:

1. $\Delta\omega_M^2 \gg \frac{1}{T_{2M}^2} \; ; \; \frac{1}{\tau_M^2}$

Equation (8) reduces to $\frac{1}{T_2} - \frac{1}{T_{2A}} = \frac{1}{T_{2p}} = \frac{P_M}{\tau_M} = \frac{1}{\tau_{H_2O}}$

2. $\frac{1}{\tau_M^2} \gg \Delta\omega_M^2 \gg \frac{1}{T_{2M}\tau_M}$

(8) becomes $\frac{1}{T_{2p}} = P_M \tau_M \Delta\omega_M^2$

3. $\frac{1}{T_{2M}^2} \gg \Delta\omega_M^2 \; ; \; \frac{1}{\tau_M^2}$

(8) becomes $\frac{1}{T_{2p}} = \frac{P_M}{\tau_M} = \frac{1}{\tau_{H_2O}}$

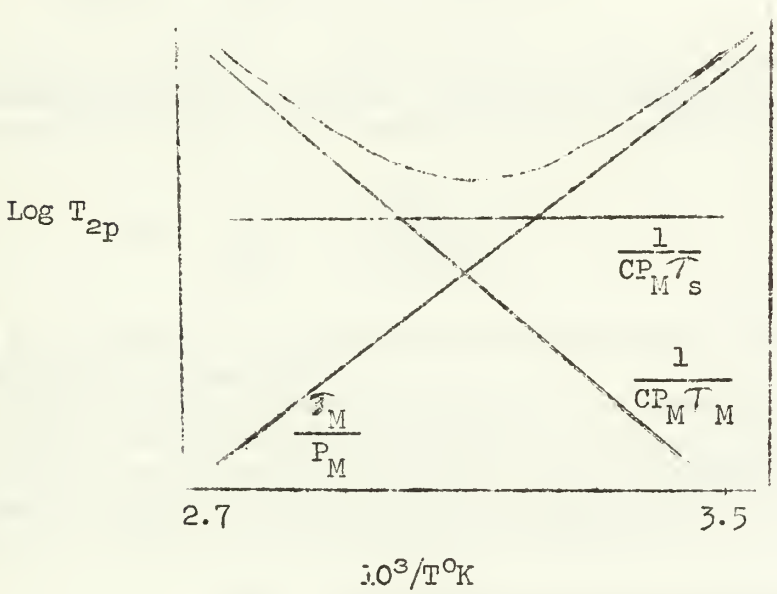
4. $\frac{1}{T_{2M}\tau_M} \gg \frac{1}{T_{2M}^2} \; ; \; \Delta\omega_M^2$

(8) becomes $\frac{1}{T_{2p}} = \frac{P_M}{T_{2M}}$

In order to determine which case applies in a given temperature range, the temperature dependence of the linewidth was studied.

To illustrate the method, consider the case of Mn(II):

The temperature dependence of log T_{2p} for Mn(II) is shown below:



In the low temperature range, the linewidth is largely determined by the chemical exchange

$$Mn(H_2O)_6^{+2} + H_2O^* \rightleftharpoons Mn(H_2O)_5H_2O^* + H_2O$$

This corresponds to cases 1 or 3. An estimate of τ_M from the slope of the curve in the low temperature region rules out case 1 because an unreasonably large coupling constant would be required.

It was determined experimentally that $T_1 \gg T_2$. This corresponds to case 2 for equations (9) and (10). Also, it was determined that the dipolar mechanism had little effect on relaxation. Thus, equation (10) becomes

$$\frac{1}{T_{2M}} = C\tau_e$$

The higher temperature range was found to be case 4. Thus $T_{2p} = \frac{T_{2M}}{P_M} = \frac{1}{P_M C \tau_e}$ with exchange controlling τ_e at high temperatures and electron relaxation dominant at intermediate temperatures.

By use of a curve-fitting process, the three lines in the above diagram were produced, and the rate constant and activation energy were calculated. The rate constant is very similar to one determined by Bernheim et.al.[3] by use of proton n.m.r. (The psuedo first order rate constant $K_1 = \frac{1}{\tau_M}$)

The remaining ions were treated in an entirely analogous fashion. The results are reported in Table 1.

B. Exchange Rates Using Proton Resonance

Pearson and Lanier[12] studied exchanges of the type

$$ML_n + L^* \rightleftharpoons ML_{n-1}L^* + L$$

where L = ammonia, ethylenediamine, glycine, N-methylglycine, and N,N-dimethylglycine in aqueous solution and anhydrous ethylene glycol. The expression they used to describe the linewidth is:

$$(14) \quad \frac{1}{T_{2p}} = \frac{P_M}{T_{2M} + \tau_M} \quad .$$

which was derived in an earlier study[16] and can be obtained from equation (8) assuming $\Delta\omega_M$ to be small.

Again the temperature dependence of the linewidth was used to determine the region in which exchange is dominant. In many cases the line-broadening was found to be relaxation controlled. When exchange was controlling, the rate was determined by studying the linewidth as a function of ligand concentration. This was done using the relationship

$\frac{1}{\tau_M} = K_1 + K_2 [L]$ where K_1 and K_2 represent the first and second order rate constants respectively. By plotting the linewidth vs. [L], K_1 and K_2 were found from the intercept and slope of the resulting curve.

The results of this study are found in Table 1.

C. Exchange Rates Using N^{14} Resonance

One example of a study using this method is that of Hunt et.al.[17,24] who determined the exchange rate for NH_3 with $Ni(NH_3)_6^{+2}$ in aqueous solution and in anhydrous ammonia. The data was treated by use of equation (14) for a temperature region where the temperature dependence of the linewidth showed exchange to be dominant. The results are listed in Table 1. As is shown, the activation energies are about the same in both aqueous and anhydrous ammonia.

A similar example is found in the study of the exchange of NCS^- with $Ni[NCS]_4[H_2O]_2^{-2}$ in aqueous solution by Murray et.al.[18]

Also, Glaeser, et.al.[23] have studied the exchange rate for NH_3 with $Co(NH_3)_6^{+2}$ by use of a modification of equation (8) and a curve-fitting process.

The results of these studies are given in Table 1.

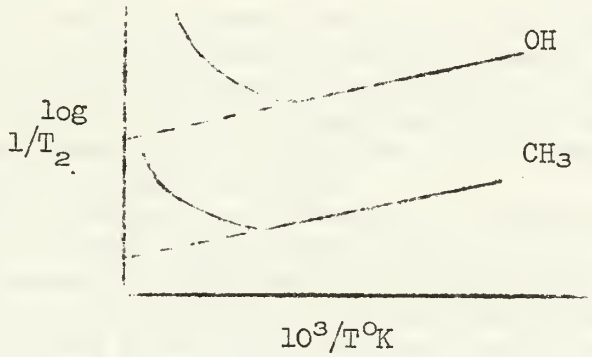
D. Studies of Slow Exchange by Proton Resonance

One can use the slow exchange approximation when distinct, non-overlapping signals are observed. The linewidth for each peak is given by (7).

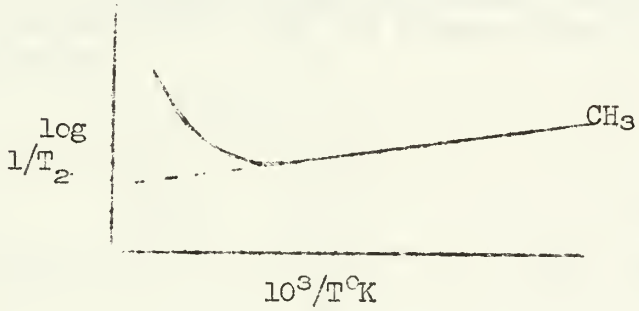
This method was used by Luz and Meiboom[13,14] to study the exchange rates of methanol complexes of Ni(II) and Co(II). It was found that at -60°C essentially no exchange occurs for either system and separate peaks are observed for complexed and free methanol protons.

Again, rates of exchange were determined by studying the temperature dependence of the line broadening. Using the peaks due to complexed methanol protons the following plots were obtained:

Co(II)



Ni(II)



From the slope of the line in the low temperature region it is clear that $\frac{1}{T_2} \approx \frac{1}{T_{2M}}$ where T_{2M} is controlled by the electron spin relaxation.

At temperatures above -40°C, the linewidth has a positive temperature coefficient and is controlled by exchange of methanol molecules between the coordination sphere and the bulk solvent.

Thus, in the temperature region controlled by exchange a value for τ_M can be found from the observed linewidth and the value of T_{2M} extrapolated from low temperatures according to the equation:

$$\frac{1}{\tau_M} = \frac{1}{T_2} - \frac{1}{T_{2M}} = K_1$$

The results are listed in Table 1

Also, Luz and Meiboom studied the exchange rates of mixed Co(II) methanol complexes by the latter method[13,25] and by use of equation (8).[26,27]

Discussion of the Results

One important consideration stemming from the above results is that of the exchange mechanisms. It has been indicated[16,19,20,22,28] that the exchange rates for octahedral complexes of the metals considered above are independent of the entering ligand. This contention is supported by a comparison of the rates for the aquo complexes obtained by Swift and Connick with the rates for the replacement of water in aquo complexes by sulfate ions and carboxylate ions obtained by Eigen.[20] The rates are remarkably similar for each metal ion, indicating that the rate determining step is dissociation of water from the metal ion.

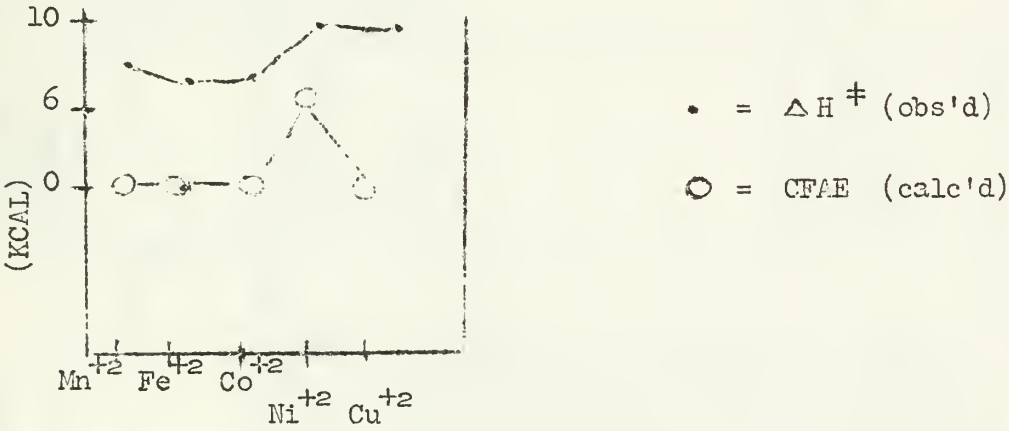
Also, the kinetic data for $Ni(NH_3)_6^{+2}$ and $Ni(NCS)_4(H_2O)_2^{-2}$ in aqueous solution fit an SN_1 type mechanism, although not unambiguously because of the presence of water.

Also, the work of Pearson and Lanier produced interesting data for exchange mechanisms involving chelating ligands. For example, all complexes of the type $CuL_2(H_2O)_2$ (where L is bidentate) showed second-order kinetics.

Octahedral complexes of bidentate ligands exhibited mixed first- and second-order kinetics except for some Ni(II) complexes whose exchange rates were too slow to measure at 25°C.

A second important consideration in connection with these results is the effect of crystal field stabilization energy on the reaction rates. Basolo and Pearson[19] suggested that the activation energy for reactions of transition metal complexes should contain a term (CFAE) due to the difference in CFSE between the original complex and the activated complex.

A good place to test this theory occurs in the data of Swift and Connick. Assuming a square pyramidal activated complex and Jahn-Teller distortions of the original octahedral complex, we can calculate a value for CFAE and compare this to the $\Delta H^{\ddagger}$ values found for the aquo complexes. This is done below.



Only the large effect for Ni^{+2} can be seen and even here the magnitude of the change in $\Delta H^{\ddagger}$ is much smaller than that in CFAE, suggesting that crystal field effects are not the major effects in determining $\Delta H^{\ddagger}$.

A similar treatment can be used on the octahedral complexes of chelating ligands which exhibited mixed first-and second-order kinetics (which Pearson and Lanier assumed was due to a solvent assisted mechanism). Assuming a 7-coordinate activated complex like that used by Hush[21], one finds that CFAE considerations predict the right order of reactivity except for Fe^{+2} which is predicted to be much more labile than it actually is.

TABLE I

	T=25°C. WATER[6]	AMMONIA	T=27°C (12) ** ETHYLENE-DIAMINE	T=27°C (12) ** GLYCINE	T=27°C (12) ** N-METHYL GLYCINE	T=27° (12) ** N,N-DIMETHYL-GLYCINE	T=27°C (12) * ETHYLENE GLYCOL	T=25°C * METHANOL	T=25°C ** (18) THIOCYANATE
Mn^{+2}	$K_1=3.1 \times 10^7$ $\Delta H^{\ddagger} = 8.1$			$Mn(gly)_2$ $K_1>1 \times 10^4$			$K_1>1.5 \times 10^6$		
Fe^{+2}	$K_1=3.2 \times 10^6$ $\Delta H^{\ddagger} = 7.7$			$Fe(gly)_2$ $K_1=2.2 \times 10^4$ $K_2=5 \times 10^4$ $\Delta H^{\ddagger} = 9.5$			$K_1>2.5 \times 10^3$		
Co^{+2}	$K_1=1.35 \times 10^4$ $\Delta H^{\ddagger} = 8.0$	(23) $Co(NH_3)_6^{+2}$ $K_1=7.2 \times 10^6$ $\Delta H^{\ddagger} = 11.2$ * T = 25°C	$Co\ en_3^{+2}$ $K_2=2.5 \times 10^3$ $\Delta H^{\ddagger} = 10.5$	$Co(gly)_3^-$ $K_1=5.7 \times 10^3$ $K_2=4.8 \times 10^2$ $\Delta H^{\ddagger} = 10$	$Co(Sarc)_3^-$ $K_1=4.2 \times 10^2$ $K_2=2.1 \times 10^3$ $\Delta H^{\ddagger} = 13$	$Co(dmg)_3^-$ $K_1=3.2 \times 10^3$ $K_2=7.3 \times 10^2$	$K_1>3.4 \times 10^3$	(13) $K_1=1.8 \times 10^4$ $\Delta H^{\ddagger}=13.8$	
Ni^{+2}	$K_1=2.7 \times 10^4$ $\Delta H^{\ddagger} = 11.6$	(12) T=27°C $Ni(NH_3)_6^{+2}$** $K_1>4.5 \times 10^4$ $Ni(NH_3)_5^{+2}$** $K_1>6.3 \times 10^4$ (17) T=25° $Ni(NH_3)_6^{+2}$** $K_1=5.6 \times 10^4$ $\Delta H^{\ddagger} = 9.5$ $Ni(NH_3)_6^{+2}$* $1.0 \times 10^5 = K_1$ $\Delta H^{\ddagger} = 11$	$Ni\ en_3^{+2}$ $K_1<2 \times 10^2$	$Ni(gly)_3^-$ $K_1<3 \times 10^2$	$Ni(Sarc)_3^-$ $K_1 = 60$ $K_2=3.3 \times 10^3$ $\Delta H^{\ddagger} = 13$	$Ni(dmg)_3^-$ $K_1 = 70$ $K_2 = 4.7 \times 10^2$ $\Delta H^{\ddagger} = 17$	$K_1=4.4 \times 10^3$	(14) $K_1=1 \times 10^3$ $\Delta H^{\ddagger} = 16.4$ or 11.2	$Ni(NCS)_4(H_2O)_2^=$ $K_1=6.9 \times 10^5$ $\Delta H^{\ddagger} = 8.6$
Cu^{+2}	$K_1=2 \times 10^6$ $\Delta H^{\ddagger} = 5$	T=27° (12) $Cu(NH_3)_4^{+2}$** $K_2 > 1.9 \times 10^7$ $Cu(NH_3)_5^{+2}$** $K_1>5.7 \times 10^6$ (12)	$Cu\ en_2^{+2}$ $K_2=1.8 \times 10^6$ $\Delta H^{\ddagger} = 7$	$Cu(gly)_2$ $K_2=2.6 \times 10^6$		$Cu(dmg)_2$ $K_1=1.3 \times 10^4$ $\Delta H^{\ddagger} = 9.5$	$K_1>1.1 \times 10^5$		

* ANHYDROUS ** AQUEOUS $\Delta H^{\ddagger}$ IS IN KCAL./MOLE K_1 IS IN SEC^{-1} K_2 IS IN $M^{-1}\ SEC^{-1}$

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TRANSITION METAL COMPLEXES AS CYCLIZATION CATALYSTS

Marcetta York November 23, 1965

INTRODUCTION

Recent developments in cyclization reactions using transition metal complexes as catalysts shall be discussed in this seminar.

The evidence compiled for metal complex catalysis in cyclization reactions points toward the involvement of the metal d-orbitals or hybrid orbitals in the excitation of the olefinic or acetylenic electrons leading to C-C bond formation. The course of the reaction has been proposed to proceed by the following scheme:

1) Pi-complex formation between the acetylenic or olefinic molecules and the transition metal of the catalysts in a geometrical orientation favoring ring closure.
2) C-C linkage as a concerted reaction forming the cyclic compound which remains on the transition metal in the form of a new pi-complex.
3) Displacement of the cyclic compound by further acetylenic or olefinic molecules which again form an intermediate complex.[1]

This seminar shall present evidence in support of this mechanism.

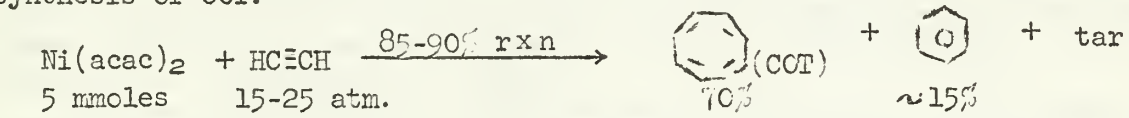
HISTORICAL PRESENTATION OF PROBLEM

In 1940 Reppe noted that acetylene, under pressure, reacted with certain nickel complexes to form cyclopolyolefins, especially cyclooctatetraene (COT).[2] He ascribed their formation to very labile acetylene-nickel complexes and proposed a chain mechanism for the reaction.

SCOPE OF THE REACTION

Various workers since Reppe have used the so-called Reppe catalysts (phosphorus modified nickel carbonyls) and related complexes in the cyclopolymerization of alkynes and alkenes. A few of these systems will be elaborated upon.

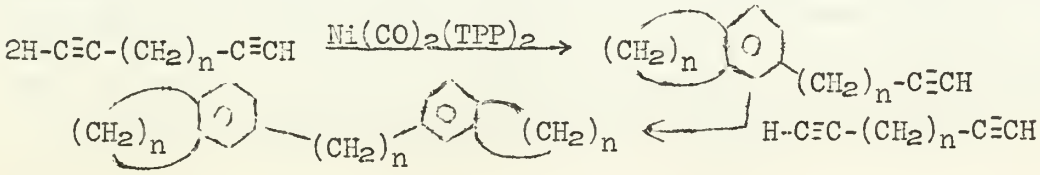
I. G.N. Schrauzer has performed a comprehensive study of Reppe's synthesis of COT.[3]



(1)

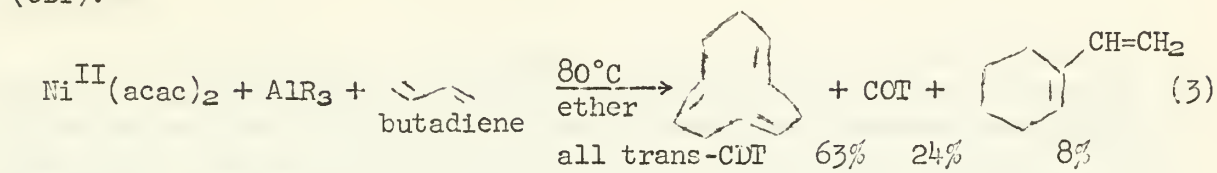
(acac= acetylacetonate)

II. Meriwether and co-workers have studied the reaction of 35 different mono- and di-substituted acetylenes with bis(triphenylphosphine)dicarbonyl nickel (0).[4,8]



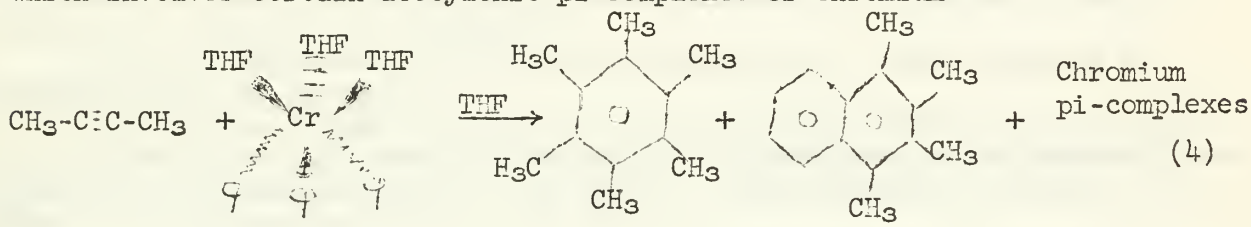
(2)

III. G. Wilke studied the following synthesis of cyclododecatriene (CDT).[5]



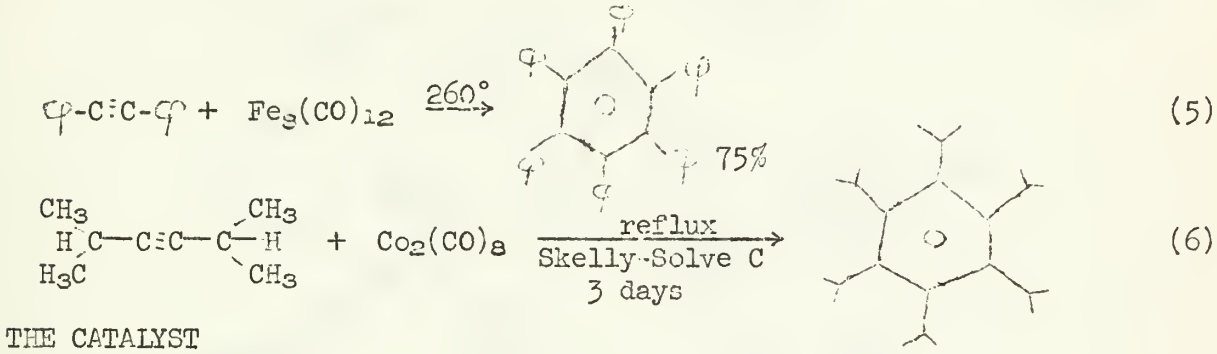
(3)

IV. Another system to be mentioned is that of Zeiss and co-workers which involves certain acetylenic pi-complexes of chromium.[6]



(4)

V. W. Hübel and C. Hoogzand have been very successful in producing benzene derivatives using metal carbonyls as catalysts.[7] The system is particularly useful in preparing the more spectacular benzene derivatives such as hexaphenylbenzene and hexaisopropylbenzene.



(5)

(6)

THE CATALYST

For the systems involving the Reppe catalysts, it has been noted that pretreatment of catalyst with unreactive disubstituted acetylenes increased the rate of reaction.[8]

As coordinating ligands, CO groups form relatively weak sigma-bonds and relatively strong pi-bonds. Therefore the replacement of CO groups to form stable complexes is to be expected only when the ligands displacing CO are of a strong pi-bonding type.

Olefins have been shown (mainly by the quantitative study of the trans effect in Pt(II) substitution reactions) to have stronger pi-bonding characteristics than nitrogen donors, sulfides, phosphines, etc., although their donor properties are relatively weak so far as sigma-bonding is concerned. Thus olefins would seem well-suited to replace carbonyl groups in metal carbonyls. Acetylenes are similar.

In the olefin $RCH{=}CH_2$, electron-donating groups (R = alkyl) make the pi-electrons more available for sigma-type bond formation; and electronegative substituents (R = Ph, F) facilitate back-donation of electrons from the metal atom by lowering the energy levels of the anti-bonding π^* molecular orbitals of the olefin. The stability of a metal-olefin (acetylene) complex thus depends on the balance of the sigma-donor and the pi-acceptor powers of the olefin, and on the nature and oxidation state of the metal.[9] Conjugation in the polyolefin favors, but is not essential for, stable metal-olefin bonding. The essential factor appears to be a suitable spatial arrangement of the C=C (or C≡C) for effective overlap with the metal hybrid orbitals.

Further elaboration of the catalyst's role and structure will be discussed in the course of considering some reactions in detail.

MECHANISM

In an investigation of the Reppe cyclic polymer synthesis (see eqn. 1), Schrauzer concludes that pi-complex intermediates are formed from which, due to the geometrical orientation of the ligands, new compounds are formed. To prove this, reactions of bisacrylonitrile nickel (0) were studied.[10] The diamagnetic complex $Ni(AN)_2(PPh_3)_2$ in which Ni has an sp^3 configuration is also formed. Therefore a complex of the type $Ni(AN)_2 \cdot 2$ alkyne should also be formed in which two molecules of the alkyne and one molecule of acrylonitrile are essentially co-planar.[10]

Various observations relating to the mechanistic scheme proposed by Schrauzer will be discussed.

G. Wilke has studied the synthesis of cyclododecatriene from butadiene using nickel acetylacetonate as the catalyst. Reactions of cyclododecatriene nickel (0) have been studied. (See Fig. 1) Wilke proposes a pi-allyl complex as the intermediate. (Fig. 2)[1,5,16]

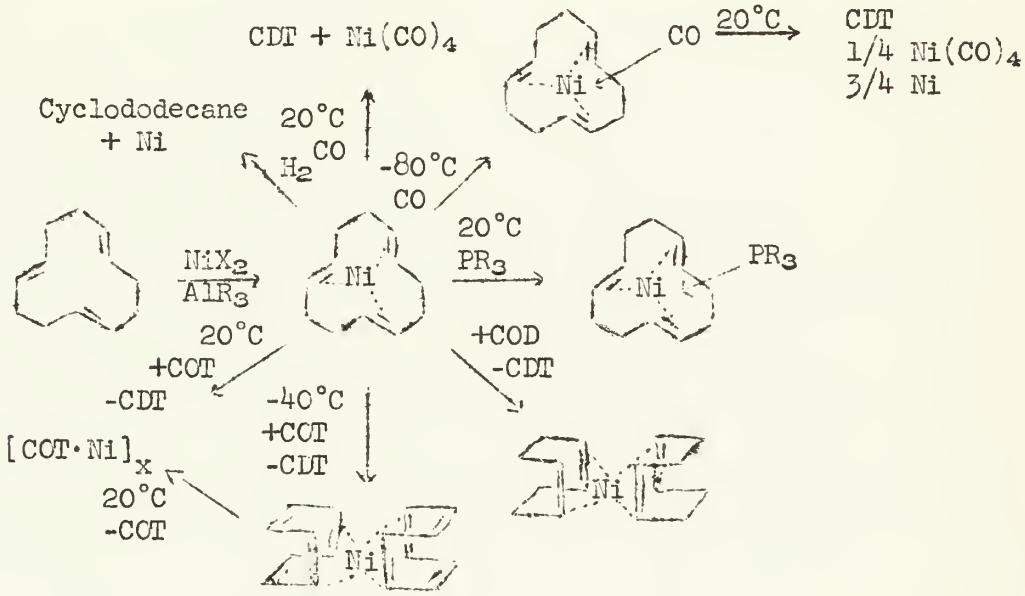


Figure 1

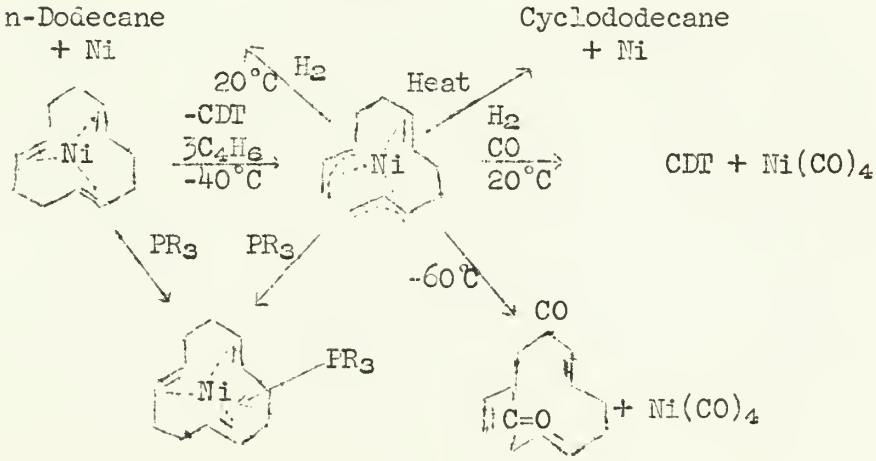


Figure 2

An analogous complex, dichloro(dodeca,-2,-6,10-triene-1,12-diyl)ruthenium(IV) has been isolated and x-ray diffraction measurements have been made.[21]

The concept of a hexacoordinated organochromium(III) compound containing replacable THF molecules has led to experiments with pi-electron systems which would not only serve as the replacing ligands on chromium but which would also be expected to react further within the confines of the hexacoordinated complex. Thus an acetylenic pi-electron system has been used to replace THF, after which the acetylenic molecules, now positioned favorably within the octahedral complex may condense into cyclic arrangements.[6]

OPPOSING MECHANISMS

Several mechanisms have been proposed to explain this type reaction.[1,4] The proposal of a cyclobutadiene intermediate is particularly interesting.[17,18,19,20,22]

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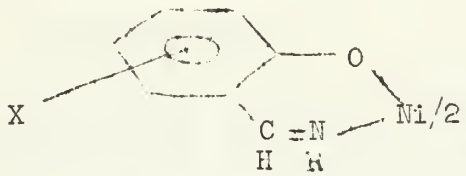
STEREOCHEMISTRY AND CONFORMATIONAL EQUILIBRIUM OF NICKEL(II) BIS(N-R-SALICYLALDIMINEATES)

James C. Hill November 30, 1965

Introduction

Various nickel(II) complexes, whether diamagnetic or paramagnetic in the solid state, show magnetic moments between 0 and 3.3 B.M. in different noncoordinating solvents. One group of such complexes, the nickel(II) bis(N-R-salicylaldimineates), is the subject of this seminar. Holm[1] and Sacconi[2] have reviewed this area through 1963, however their bibliographies are not complete and some conclusions are incorrect.

The general form of these complexes is:



where R will be some carbon substituent and X an inorganic or organic substituent.

Review of Earlier Work

Since the stereochemistry and the conformational equilibrium of these complexes is largely dependent upon R and to some extent X, the complexes will be divided according to R, where R is methyl, n-alkyl, alpha-branched and aryl.

R = Methyl

Pfeiffer and Glasser first prepared the methyl complex[3], but it was Klemm and Raddatz[4] who first reported two forms, a diamagnetic and an unstable paramagnetic, of Ni(II) bis(N-methylsalicylaldimineate). The diamagnetic complex exists in a square planar monoclinic[5] and an orthorhombic[6,7] form. Studies by various workers showed that the diamagnetic form dissolved in such solvents as chloroform[8,12], benzene[8-10], toluene[9-10], and pyridine[8,10,13] showed magnetic moments between 1.4 and 3.1 B.M. The diamagnetic form could be heated to a paramagnetic form.[14-18] The spectra of the complex in different solvents was temperature dependent.[9,10,19-23]

Three explanations were proposed to explain the above phenomena; a planar and tetrahedral equilibrium in solution[8,9,16,19], a ligand field model which assumes individual planar molecules and a thermally regulated singlet-triplet distribution of molecules where the separation is a function of the solvent[24-27], and an equilibrium involving associated and planar molecules.[15,20,28] The first was discarded by Sacconi, et.al.[10], and the second ruled out when Ferguson[20], Holm[28], and Harris[15] carried out molecular weight measurements in various solvents and found the complex to be partially

associated. The accepted explanation for the anomalous magnetic behavior of Ni(II) bis(N-methylsalicylaldimineate) is an associated, planar equilibrium with the proportion of planar molecules increasing with temperature.

R = n-alkyl

All the complexes studied were diamagnetic and square planar in the solid state and with magnetic moments varying between 0.29 and 1.06 B.M. in chloroform and benzene.[10,28-31] In the molten state and in dibutyl phthalate the magnetic susceptibility of the ethyl, propyl, and octyl complexes increased with temperature.[29] The molecular weights in freezing and boiling benzene showed little or no association.[29,30-31] The electronic spectra of these complexes in solution above 80°C has a band around 6,700 cm^{-1}, characteristic of the isopropyl complex which was known to exist in a tetrahedral form, and below 80°C a band at 16,000 cm^{-1}, diagnostic of the planar specie, was the primary band.[32-34] The n-alkyl complexes seem to undergo a planar, tetrahedral equilibrium with the percentage of tetrahedral species increasing with temperature.

R = alpha-branched

The complexes where R is isopropyl and t-butyl are paramagnetic and tetrahedral, while sec.-butyl is diamagnetic and planar in the solid state.[32,34,35,36] The isopropyl complex has a pseudo-tetrahedral structure as shown by X-Ray studies.[37] The complexes where R is the cyclic groups C_3H_5, C_5H_9, and C_6H_{11} are all diamagnetic and planar. The data in solution supported a planar, tetrahedral equilibrium except for the cyclopentyl complex which was associated.

R = aryl

Holm has reported that the para and ortho substituted aryl complexes and the 3-substituted complexes can be both paramagnetic and diamagnetic in the solid state, while all the meta substituted aryl complexes are paramagnetic.[38] Zelentsov, et. al., found similar results.[39] The diamagnetic species seem to be planar from their reflectance spectra, while the structure of the solid paramagnetic species is unclear.[40] The complexes show various magnetic moments in solvents. Complexes which were paramagnetic in solution were extensively associated up to 70°C.[38] Above 80°C a temperature dependent electronic spectra study done by Sacconi showed bands appearing at 6,700 cm^{-1} and 11,100 cm^{-1}, indicating formation of tetrahedral species.[40] Sacconi concluded that an associated, planar, tetrahedral equilibrium existed for the complexes which showed paramagnetism in solution, and planar species existed for the nonparamagnetic ones.

Recent Complexes

Chakravorty and Holm studied a series of three isomeric Ni(II) bis(o-hydroxynaphthaldimineate) complexes where R was isopropyl, t-butyl and 3-pentyl.[41] They exist either as diamagnetic or paramagnetic solids. In chloroform solution, the effective magnetic moments are in the range 0 to 3.3 B.M. The electronic and NMR spectra of these complexes in solution substantiated the formation of tetrahedral species for the diamagnetic solids and planar species for the paramagnetic solids. With the absence of association, the existence of a planar, tetrahedral equilibrium was established.

Chakravorty, Fennessey and Holm looked at a series of Ni(II) bis(N-R-salicylaldimineate) complexes, where R had a terminal methoxyl or hydroxyl group capable of coordination.[42] Those complexes with a branched alkyl chain portion and with either a terminal methoxyl (A) or hydroxyl (B) group are paramagnetic and octahedral in the solid state. Those with a straight chain alkyl group and a terminal methoxyl group (C) are diamagnetic and planar. In chloroform solution, the ligand field spectra and proton NMR contact shifts showed that in the temperature range -40°C to 50°C discrete octahedral, planar and tetrahedral species were in equilibrium for complexes A, complexes C existed as planar species in solution, while complexes B were insoluble.

Sacconi, Nannelli, and Campigli,[43] and Sacconi, Nannelli, Nardi and Campigli,[44] studied 67 complexes of Ni(II) bis(N-R-salicylaldimineate) where R is $-CH_2CH_2N(R'R'')$. The complexes are pseudo-octahedral and mononuclear in both noncoordinating solvents and in the solid state when R'= H and R''= n-alkyl and benzyl.[43] When R'= H and R''= ortho substituted phenyl, the complexes are trans square planar and diamagnetic in the solid state and exist in an octahedral, planar equilibrium in noncoordinating solvents.[43] With R'= H and R''= para substituted phenyl, the complexes, depending upon X are either mononuclear octahedral or square planar in the solid state and show an octahedral, planar equilibrium in solution.[43] When R'= phenyl and R''= methyl or phenyl, the complexes are trans planar both in the solid state and in solution.[43] If N(R'R'') is the dimethylamino or pyrrolidino group, the complexes are distorted octahedrons.[44] When N(R'R'') is the piperidino group they are square planar.[44] When N(R'R'')is the diethylamino group the complexes are square planar or octahedral, depending on X, except when X = 3-Cl, 5-Cl and 3,4 benzo in which case they are paramagnetic and five coordinate.[44] A complete X-ray analysis of the 5-Cl complex showed the Ni atom to be five coordinate with the structure resembling a distorted square pyramid.[45] Spectral studies indicated most of the complexes studied by Sacconi, Nannelli, Nardi and Campigli are involved in an octahedral, five coordinate, and planar equilibrium with the planar form favored above 30°C.[44]

A penta-coordinated distorted trigonal bipyramid of Ni(II) bis(N-methylsalicylaldimineate) complex was found by Sacconi, Ciampolini, and Speroni in a solid solution of Zn(II) and Ni(II) bis(N-methylsalicylaldimineate).[46]

NMR Studies

The behavior of these Schiff base complexes is similar to that exhibited by N,N disubstituted aminotroponeimine Ni(II) complexes[47-48] which show high and low field resonance shifts from the free ligands. Assuming the rate of structural interconversion of tetrahedral and planar molecules is sufficiently rapid, the observed contact shifts are averaged over the singlet and triplet state and the free energy of the equilibrium is related to the proton contact shift by:[47-52]

$$\frac{\Delta f_i}{f} = -a_i \frac{\gamma_e}{\gamma_H} g\beta \frac{S(S+1)}{2SkT} \left[e^{\frac{\Delta F}{RT}} + 3 \right]^{-1}$$

where Δf_i is the observed contact shift for the ith proton, f is the spectrophotometer frequency, a_i is the hyperfine interaction constant for the ith proton, and $\frac{\gamma_e}{\gamma_H}$ is the gyromagnetic ratio of the electron and the proton.

Eaton, et.al., in a note applied their results to N-meta tolyl complexes.[53] The proton contact shifts observed were in agreement with that qualitatively predicted by valence bond considerations. The results supported delocalization of the fractional unpaired electron by d_{π}-p_{π} bonding of the ligand with nickel. Comparison of experimental with calculated spin densities suggested 1/60 of an electron is transferred.

The first extensive NMR studies done by Holm et.al.,[54] on Ni(II) bis(N-sec.-alkylsalicylaldimineate) complexes supported a planar, tetrahedral equilibrium above 40°C, but below 40°C a plot of Δ F versus T was nonlinear. Solute association was assumed to occur below 40°C. Complexes containing optically active groups formed from racemic amines showed two sets of resonance signals, one from the meso complex and one from the active complexes. This was in agreement with a previous note by these authors.[55] Thermodynamic parameters were calculated from contact shift data and differences in free energy between the active and meso forms ranged between 12 and 80 cal./mole at 60°C.

Chakravorty and Holm[39] carried out studies on bis(o-hydroxynaphthaldimine) complexes, and observed contact shifts. Temperature dependent proton contact studies indicated no association in the temperature range -20°C to 20°C. Coupling constants for the naphthalene ring compared favorably with those of a recent analysis of the naphthalene spectrum.

Chakravorty and Holm also investigated the equilibrium of mixed ligand complexes.[56] They observed resonance signals for the initially pure complexes and the mixed complexes after equilibrium was obtained. They suggest a model for ligand exchange.

Chakravorty, et.al.,[42] used the NMR to study the octahedral, tetrahedral planar equilibrium of Ni(II) bis(N-R-salicylaldimineate) where R is a branched alkyl chain with a terminal methoxyl group. For some of the complexes a linear dependence of the contact shifts versus 1/T was found in the temperature range -40°C to 0°C, supporting the presence of monomeric octahedral species. At higher temperatures, the increased displacement of contact shifts supported the onset of a planar, tetrahedral equilibrium. Pairs of signals were observed for the diasteromeric complexes.

ADDENDUM

W. Horrocks, Jr., in a communication to the editor, J. Am. Chem. Soc., 87, 3779 (1965), pointed out that the equation given in the NMR section of this abstract and other papers is incorrect and should be:

$$\frac{\Delta f_i}{f} = \frac{-a_i}{2S} \frac{\gamma_e}{\gamma_H} g \beta \frac{S(S+1)}{3kT} \left[e^{\frac{\Delta F}{RT}} + 1 \right]^{-1}.$$

ΔF values given in the journals and this seminar are too high by RT ln 3 and ΔS values are too low by R ln 3.

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MECHANISM OF RACEMIZATION OF OCTAHEDRAL COMPLEXES WITH BIDENTATE LIGANDS

Linda Donlon December 7, 1965

INTRODUCTION

A perusal of the literature indicates that there is a paucity of definitive experimental evidence pertaining to the racemization of octahedral complexes containing bidentate ligands, so that to discuss each complex for which kinetic data has been reported would be of limited value. Instead, it seemed to be much more interesting to examine the problem from the standpoint of experimental approaches — their weaknesses in addition to the valid information which each might yield toward ascertaining a mechanism for a particular complex species.

PROPOSED MECHANISMS

Four distinct mechanisms have been proposed for the thermal racemization of octahedral complexes containing bidentate ligands — these are commonly referred to as the bond rupture, dissociative, rhombic twist and trigonal twist mechanisms (Fig. 1). Mechanisms proposed for racemizations involving electron transfer or heterogeneous catalysis will not be considered.

The bond rupture mechanism proposed by Werner[1] involves the momentary rupture of a metal-ligand bond, forming an intermediate which might be a trigonal bipyramid, a square pyramid or an octahedron with the vacated coordination position occupied by a solvent molecule. The trigonal bipyramidal structure is the more frequently formulated intermediate in discussions of the bond rupture mechanism, and reformation of the ruptured bond will have an equal probability of retention and inversion of configuration.

The bond dissociation mechanism, as formulated by Thomas[2], attributes racemization to detachment of one of the three bidentate ligands and formation of a planar intermediate. More probable is an octahedral intermediate (with the two vacated positions filled by solvent molecules) which is either symmetrical or racemizes exceedingly rapidly.

Rây and Dutt[3] proposed an intramolecular twisting mechanism which is referred to as the rhombic twist in accord with the pseudo-rhombic symmetry of the transition state. This mechanism is best visualized as holding one chelate ring unchanged and moving the other two, in opposite directions, 90° in their own planes.

More recently, Bailar[4] proposed a second intramolecular twisting mechanism which has, in reference to the trigonal symmetry of the transition state, been termed the trigonal twist. Racemization is achieved by twisting one triangular face of the octahedron through an angle of 120° with respect to the triangular face opposite and parallel to it.

CLASSICAL CHEMICAL TECHNIQUES

Heretofore, the most intensively studied systems have been the tris complexes with oxalate, dipyridyl or 1,10-phenanthroline as the bidentate

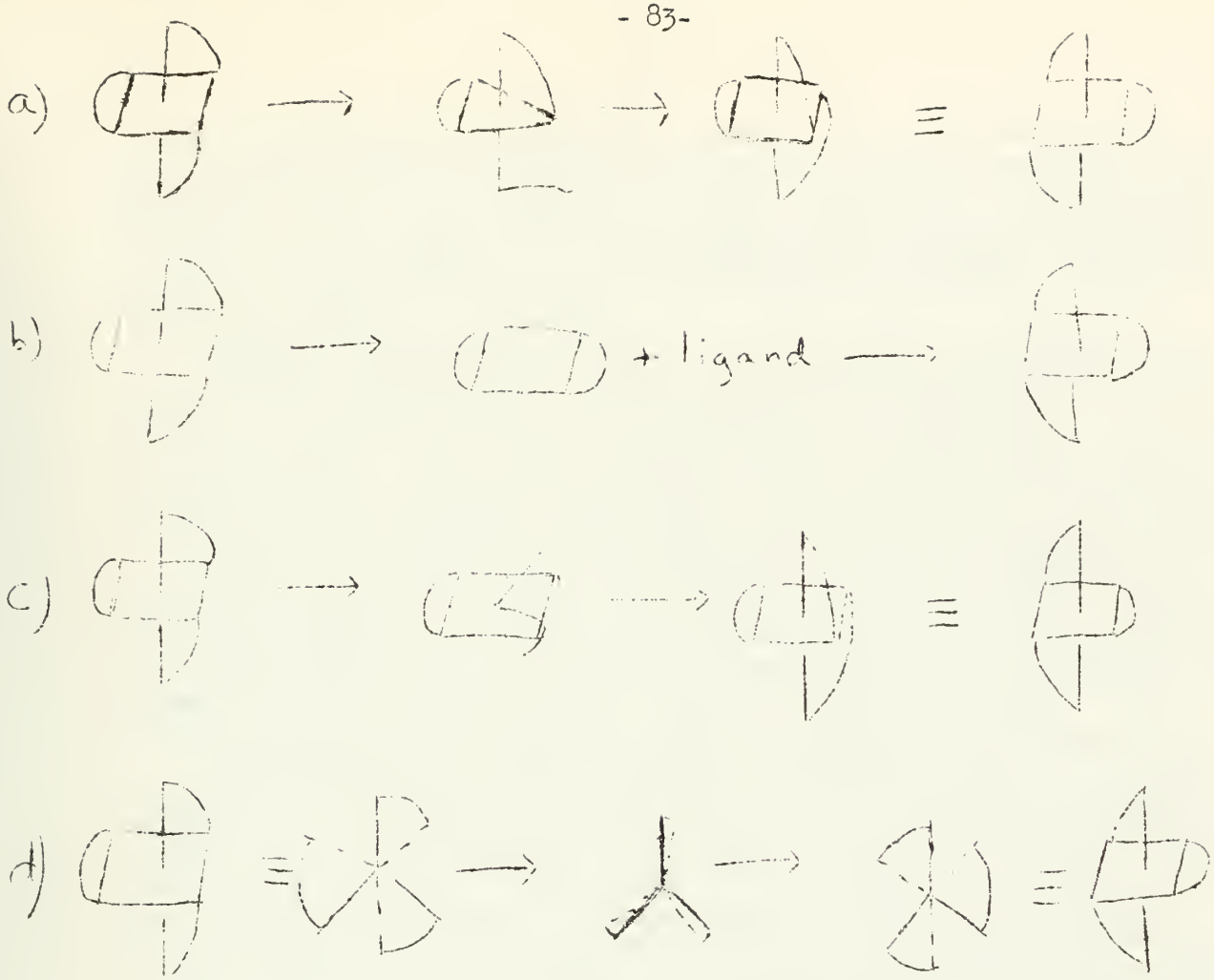

Fig. 1: Racemization Mechanisms

(a) Bond rupture, (b) Dissociative, (c) Rhombic twist and (d) Trigonal twist

ligand. Although classical chemical manipulations would not be expected to distinguish the more subtle aspects of the four proposed mechanisms, one might hope to be able to differentiate between an intermolecular and an intramolecular mechanism. As illustrative examples, the tris-phenanthroline Ni(II), which is thought to racemize intermolecularly, and the tris-oxalato Cr(III) and Co(III) ions, which are thought to racemize intramolecularly, will be considered in some detail.

The $Ni(phen)_3^{+2}$ system received intensive study from Basolo[5] and Dwyer[6-8] and their coworkers. Because of the good agreement between the rate of dissociation[5] in acid solution and racemization[5,9] and exchange rates in water and non-aqueous solvents it is commonly concluded[10-12] that the mechanism involved in racemization is the intermolecular, dissociative mechanism.

However, Davies and Dwyer[8] noted that the E_a and PZ values (from the Arrhenius equation: $k = PZe^{\frac{-E_a}{RT}}$) for racemization varied between quite narrow limits for the complex in a wide variety of solvents, and suggested that an intramolecular mechanism is operative. Having concluded from

exchange data[9] that the dissociative mechanism is operative in water, ethanol and methanol, Broomhead[13] attempted to show the constancy of this mechanism in all of the non-aqueous results reported by Davies and Dwyer. Broomhead constructed $\Delta H^{\ddagger}$ vs $\Delta S^{\ddagger}$ plots of the data and believed their linearity to be indicative of a purportedly valid isokinetic relationship advanced by Leffler[14]. Leffler's work, however, has since been most elegantly refuted by Petersen[15].

Although exchange data provide quite reasonable grounds for a supposition of a dissociative mechanism, there is another conceivable mechanism which is consistent with all of the experimental observations. If a twisting motion were, in the rate determining step, to produce an activated symmetrical intermediate which was more susceptible to chemical attack than the more stable octahedral configuration, then attack by H^+ could lead to dissociation and attack by phenanthroline could result in ligand exchange.

Fay[16] has noted that the calculated E_a for the bond rupture and dissociative mechanisms decrease very rapidly as $\underline{c}$ (the electronic charge on the coordinating atom of the ligand) increases from 0.5 to 1.0, while the activation energies for the twisting mechanisms gradually increase. This suggests that twisting mechanisms are more likely for cationic complexes, whereas rupture of bonds is more likely for anionic complexes.

During the past 50 years a number of chemical studies[1,17-23] of the $Co(C_2O_4)_3^{-3}$ and $Cr(C_2O_4)_3^{-3}$ ions have been done, but the more compelling evidence for an intramolecular mechanism is that provided by exchange data. Long, using C^{11}-oxalate showed there was no exchange in aqueous solution with either $Cr(C_2O_4)_3^{-3}$ [24] or $Co(C_2O_4)_3^{-3}$ [25] during a time interval sufficient for extensive racemization, thus precluding a dissociative mechanism. Long's results have been verified by others[26,27] using the more stable C^{13} and C^{14} isotopes, and in addition it has been shown[27] that H_2O^{18} exchanges oxygen with all 12 oxygens on the $Cr(C_2O_4)_3^{-3}$ complex. This suggests the bond rupture mechanism although it should be noted that racemization is faster than oxygen exchange. Calculations[28] of energies required to form the possible racemization intermediates indicate that the trigonal bipyramid is favored substantially over the trigonal prism or tetragonal pyramid. However, these calculations have been criticized[29] because they neglected to consider any changes in crystal field stabilization energy and bond lengths in the activated complexes.

Circular dichroism spectra[30] of $(-)Co(C_2O_4)_3^{-3}$ imply that in solution the ion exists as a mixture of $Co(C_2O_4)_3^{-3}$ and $Co(C_2O_4)_2(OH)(OC_2O_3H)^{-3}$.

PRESSURE STUDIES

On the basis of calculations indicating that a trigonal prism intermediate would be of smaller volume than the octahedron, Schmulbach[31,32] has studied the effect of pressure on the racemization of $K_3[Co(C_2O_4)_3]$, $[Fe(phen)_3](ClO_4)_2$ and $[Ni(phen)_3](ClO_4)_2$. Although the rate of racemization does increase with increasing pressure, the reported $\Delta V^{\ddagger}$ are nearly zero. Since the experiments were done in the solid state, these results are probably inconclusive.

Pertinent to this is a report[33] on the effect of pressure on the spectra of Ni(II) complexes, including $Ni(phen)_3^{+2}$. Increasing pressure increased D_q, implying an increase in the degree of covalency between the metal atom and its ligands.

NUCLEAR MAGNETIC RESONANCE STUDIES

Perhaps the most ingenious and fruitful approach was that utilizing NMR information. Fay and Piper[34] observed that if the optically active complex were to contain unsymmetrical ligands, racemization would or would not be accompanied by concomitant cis-trans isomerization, depending upon the mechanism. Assuming no prohibitive steric inhibitions, the dissociative, rhombic twist and bond rupture mechanisms can result in both racemization and isomerization. The trigonal twist mechanism, however, interconverts optical antipodes, but fails to interconvert cis-trans isomers. Fay and Piper studied the trifluoroacetylacetonates of Al, Ga, In, Co and Rh. A cis isomer has C_3 symmetry and thus the trifluoromethyls will show only a single fluorine resonance. A trans isomer, however, has no symmetry and the trifluoromethyl groups are nonequivalent, exhibiting three fluorine resonances in the absence of exchange. The coalescence of NMR signals due to rapid exchange of nuclei between magnetically nonequivalent sites is indicative of very rapid racemization and isomerization. The dissociative, rhombic twist and bond rupture mechanisms all provide a path for the exchange of the four magnetically nonequivalent groups of the cis and trans isomers and hence would be consistent with the coalescence of four resonance lines. In the presence of excess trifluoroacetylacetone, the dissociative mechanism predicts the coalescence of the trifluoroacetylacetone resonance with the resonance due to the complex. The trigonal twist interchanges the environments of two of the trifluoromethyl groups of a trans isomer, but leaves the third trifluoromethyl of the trans isomer and the trifluoromethyls of a cis isomer unaffected. Therefore, in a cis-trans mixture, the trigonal twist predicts the coalescence of just two of the four lines in the NMR spectrum. Combination of NMR results and point charge ionic model calculations led Fay and Piper to the following conclusions: (1) The trigonal twist may be eliminated for Al, Ga, and In trifluoroacetylacetonates and also for the racemization of cis-chromium benzoylacetonate. (2) The activation energy for the trigonal twist is higher than for the rhombic twist except for metal ions having crystal field stabilization energy. (3) The stereochemical rearrangements of Al, Ga, In and Co trifluoroacetylacetonates and Cr benzoylacetonate probably proceed via the bond rupture mechanism.

The only ambiguity in the trifluoroacetylacetonate systems was the inability to distinguish, experimentally, between the rhombic twist and bond rupture mechanisms. Klabunde[35] did an NMR study of tris-[3-acetyl (D-labeled)2,4-pentanediono]cobalt(III) in an attempt to differentiate between mechanisms involving one or no bond rupture since if one Co-O bond breaks completely, either the D-labeled acetyl group or the original acetyl group could be used to reform the chelate ring. Preliminary experiments indicated a bond rupture mechanism.

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OXYGEN BRIDGED COMPOUNDS OF Cr(III)

David A. Rowley December 14, 1965

I. Introduction

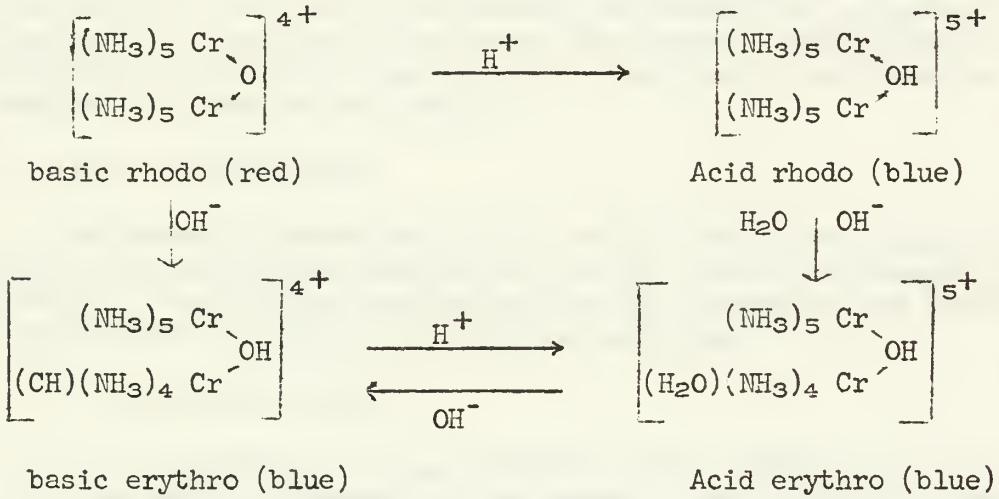
Bridging compounds have been receiving increased attention in the recent literature, and the two most important reasons for this are: (1) interest in these compounds as proposed intermediates for reaction mechanisms[1]; and (2) interest in their magnetic behavior[2]. Bridging compounds may be divided into classes[3,13]:

(1) metal nuclei bridged by a single atom i.e. -O-, -N-, $\diagdown O \diagdown$ H;

(2) metal nuclei bridged by more than one atom i.e. EDTA, $C_2O_4^{=}$.

II. Scope of the Seminar

This seminar will discuss the properties of and theories proposed to explain the nature of the rhodo and erythro compounds of Cr(III).



III. Preparation and Properties

These compounds were first prepared by Jørgensen[4] in 1882 by aerative oxidation of Cr(II) in a strongly buffered ammonical solution. The physical properties such as rates of hydrolysis[5,6,7] and pK for these complexes have been studied. It has been found that the rate of hydrolysis of the basic rhodo salt to the basic erythro salt appears to be independent of pH, but decreases very slightly at high pH.

Complexes of the form $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_4X]^{n+}$, where X is NH_3, OH, H_2O, F, Cl, and SCN, have been prepared by Schwartzenbach and Magyar[7]. As one would expect, the group X exerts a strong influence on the acidity of the bridging proton. The order for the pK is OH > F > Cl > SCN > NH_3. These authors have also reported the spectra for these compounds.

Perhaps the most extensively studied property of these complexes is their magnetic character[2,5,8-11]. The magnetic moments at room temperature of the basic erythro, acid erythro, and acid rhodo indicate three unpaired electrons

and are only slightly depressed from their mononuclear counterparts[19]. The slight decrease has been attributed to some type of exchange mechanism[10]. When one looks at the magnetic moment of the basic rhodo salt this indicates less than one unpaired electron per Chromium atom.

The electronic spectra[7,11] for these compounds indicates that the acid rhodo and the acid and basic erythro salts are similar to their mononuclear counterparts, but the basic rhodo salt has very different features.

Powder patterns for these four compounds indicate that the acid rhodo and the acid and basic erythro compounds are similar, but the basic rhodo complex is different[5]. Because of π bonding, between the Chromium and the oxygen, the rhodo complex is assumed to have a linear Cr-O-Cr entity[10]. In the Cr-OH-Cr compounds the bond angle is most probably 120°.

IV. Interpretation of the Magnetic and Spectral Properties

There are at least two possible models for explaining the properties of these complexes:

(1) considering the overall symmetry of the molecule;
(2) considering the site symmetry of a single Cr(III) ion.

A. Acid rhodo, acid erythro and basic erythro complexes

The spectra and magnetism of the above compounds is very close to that found for its mononuclear counterparts when one assumes an O_h field and uses the idea of an average environment as suggested by Jørgensen[20]. The slight decrease in the magnetic moment from the mononuclear counterparts may be due to some type of exchange as suggested by Earnshaw and Lewis[10].

B. Basic rhodo Chromium

The magnetic properties of this salt indicate less than one unpaired electron at room temperature and at ~ 125°K, it becomes diamagnetic. Two different molecular orbital approaches have been given in an attempt to explain its magnetic character.

(1) Dunitz and Orgel[13]

By considering the C_{4v} symmetry of the Cr(III) atoms and the assumed D_{4h} symmetry of the molecule, the following order of M.O.'s was obtained: $E_u^b[E_gB_{2g}B_{2u}]E_u^a$, where the orbitals in the brackets are approximately degenerate. This leads to an electronic configuration of: $(E_u^b)^4[(E_g)^4(B_{2g})^1(B_{2u})^1](E_g)^0$. This explains the moment at room temperature, but not at lower temperature. Ballhausen has suggested[14] that perhaps the configuration might be $(E_u^b)^4[(E_g)^4(B_{2g})^2(B_{2u})](E_u^a)$. Since no quantitative calculations were done, no definite conclusions can be drawn.

(2) Jezowska-Trzebiatowska and Wojciechowski[11,16]

These authors have considered the C_{4v} symmetry of each chromium atom, the D_{4h} symmetry of the molecule and the C_2 symmetry of the oxygen atom. They obtained the following order of M.O.'s: $E_g^b\ E_uA_{1g}A_{2u}E_g^a$. Thus the basic rhodo salt would have the configuration $(E_g^b)^4(E_u)^4(A_{1g})^2(A_{2u})(E_g^a)$. At higher temperatures some excited states could become populated, which could account for the increase in the magnetic moment with increasing temperature.

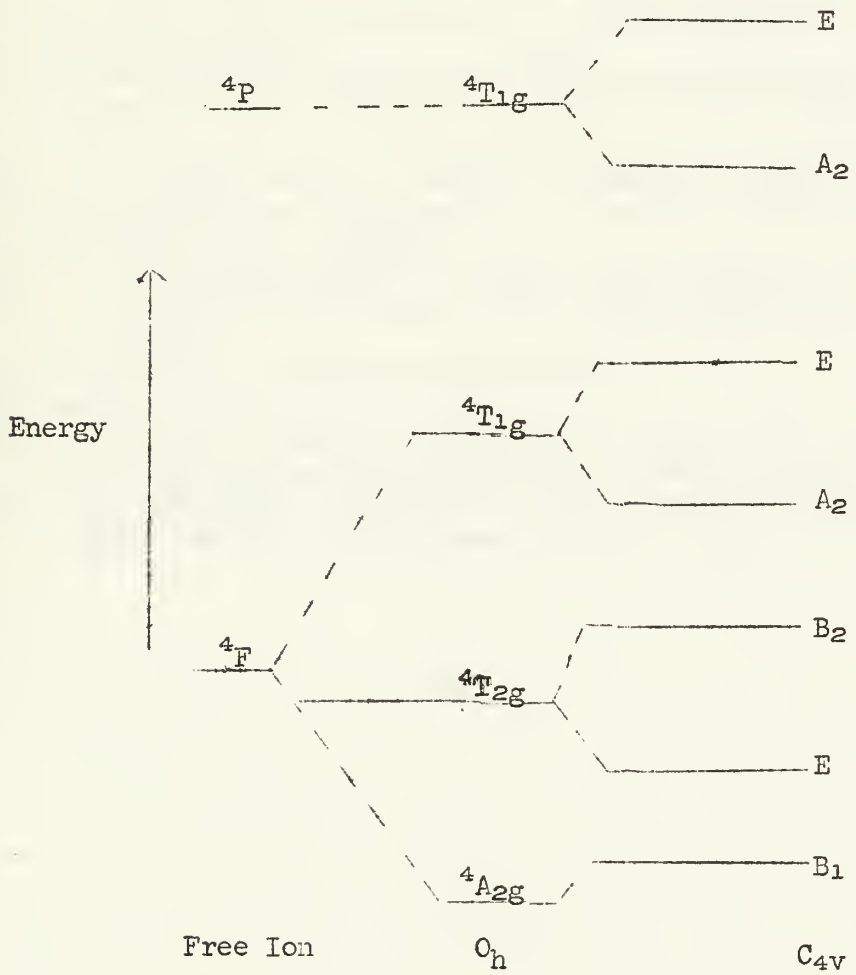
There has been little attempt to explain the spectra of this complex. There seems to be at least two reasonable approaches to this problem.

(1) Molecular orbital theory

This complex is similar to the Vanadyl complex. Use of the molecular orbital diagram for this complex could lead to reasonable interpretation of the spectra[15]. We would consider the molecule as $(NH_3)_5Cr\text{-}O\text{-}X$. One possible explanation that seems to be consistent with the spectra will be discussed.

(2) Crystal field theory

If we consider the complex as C_{4v}, the splitting of the quartets is as shown below[17]



The doublets are unaffected in first order perturbation theory. The spectra will be discussed in terms of this diagram and the splitting parameters, B, Dq, Ds, and Dt.

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STRUCTURAL ASPECTS OF ORGANOSELENIUM COMPOUNDS

Mary Leung December 20, 1965

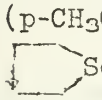
Introduction

Structural aspects of compounds involving Se-C bonds will be considered in this seminar. In Tables I and II, bond lengths and bond angles of some structurally known examples have been tabulated.

Table I. Two-Bonded-Se Compounds

Compound	C-Se(Å)	∠ XSeY	CSeSe/SeSeC	Method Used	Ref.
OCSe	1.709	180° (d)	-----	M.W.	(1)
$(CF_3)_2Se$	1.96	104.4°	-----	E.D.	(2)
$(C_6H_5)_2Se_2$	1.93	106°	82°	X-Ray	(3)
$Se(SeCN)_2$	1.83	101°	94°(a)	"	(4)
$Se(CN)_2$	1.86	119°	-----	"	(5)
$(p\text{-}ClC_6H_4)_2Se_2$	1.93	101°	74.5°	"	(6)
$(p\text{-}CH_3C_6H_4)_2Se$	1.93	106°	-----	"	(7)

Table II. Four-Bonded-Se Compounds

Compound	C-Se(Å)	∠ CSeC	∠ XSeX	Method Used	Ref.
$(p\text{-}CH_3C_6H_4)_2SeCl_2$	1.93	106.5°	177.5°	X-Ray	(8)
$(p\text{-}CH_3C_6H_4)_2SeBr_2$	1.95	108°	177°	"	"
 $Se \cdot I_2$ (b)	1.96	93.2°	167.2° (c)	"	(9)

(a) This is the angle of SeSeSe/SeSeC.
(b) This compound is included here for reasons given later in the abstract.
(c) Angle formed by iodine-selenium-iodine (of a neighboring molecule).
(d) ∠OCSe

A few remarks can be made with regard to these data. Se-C bond lengths vary over not too small a range. 1.71 Å is usually taken to be the double bond length and 1.96Å, the single bond length. Other than the linear molecule carbonyl selenium, Se-valency angles in the two-bonded-Se compounds have values smaller than 109°, suggesting a close approach to sp^3 hybrid bond type. Four-bonded-Se compounds, however, appear to be trigonal bipyramidal in configuration.

Dihedral Angles

A perhaps more interesting feature is the Se dihedral angle. A dihedral angle is an angle between two planes. For a diselenide, this angle is Θ in Fig. 1.

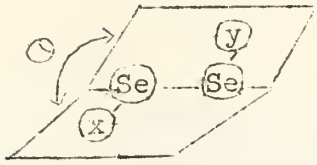
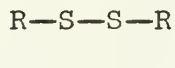


Fig. 1

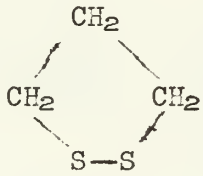
No theoretical treatment has been given to the Se dihedral angle. With H_2O_2 though, Penney and Sutherland[10], assuming only oxygen p orbitals were used in bonding, showed that the predominant steric factor governing the dihedral angle is repulsion between unpaired electrons on each oxygen atom. The subsequently calculated $\Theta = 100°$ corresponding to a minimum potential energy for the molecule. Lassettre and Dean[11], taking into account interactions between O-H bonds, between O-H bond and lone pair, as well as between lone pairs, obtained Θ in the range 94-113°. Later, x-ray study of solid H_2O_2 at -20° gave $\Theta = 94°$ [12].

With disulfides, a molecular orbital treatment of the 3pπ interaction has been performed[13]. In valence bond language, Pauling[14] suggested that the rotation barrier about the S-S bond is mainly due to 3pπ sulfur interactions. Accordingly, repulsion is at its maximum when the orbitals are parallel, but minimum when they are orthogonal to each other. Such an electronic picture is equivalent to differentiating between a dihedral angle of 0° and that of 90°. This description leads to a simple twofold rotation barrier the height of which has been calculated to about 12 $\pm$ 2 kcal/mole[15,16]. One may note that experimental values of Θ for disulfides (I) are indeed close to 90°[17].

Bergson's molecular orbital calculation[13] was prompted by observations of another compound, 1,2-dithiolane (II).



(I)



(II)

It is known that normal disulfides are colorless (absorption maximum at 2500Å) whereas dithiolane is yellow (absorption maximum at 3300Å)[18]. Then making two assumptions: first, that there are pure 3p orbitals on the sulfur atoms, and secondly, that the dihedral angle in 1,2-dithiolane is 0°, Bergson calculated total energy of the 3pπ system for $\Theta = 0°$ and $\Theta = 90°$, and correlated conformation changes to observed UV absorption data of the two compounds. Expected excitation energy and absorption maximum were then calculated by taking the value of 12 $\pm$ 2 kcal/mole[15,16] as repulsion between 3p π electrons. His results are shown in Tables III and IV.

Table III

N	Configuration	$\Delta E_N = E_N^{0} - E_N^{90}$	Numerical Value of ΔE_N	Sign of ΔE_N	in the most Stable Conformation
3	$(\phi_+)^2(\phi_-)^1$	$\frac{1-3S}{1-S^2}(\beta - E_A S)$	$0.624\,\gamma$	negative	0°
4	$(\phi_+)^2(\phi_-)^2$	$\frac{4S}{1-S^2}(E_A S - \beta)$	$-0.524\,\gamma$	positive	90°

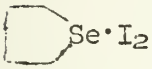
$\phi_\pm = \phi_A \pm \phi_B \qquad E_A = \int \phi_A H_{eff} \phi_A \, dv \qquad \beta = \int \phi_A H_{eff} \phi_B \, dv$

$S = \int \phi_A \phi_B dv \qquad \gamma = \beta - E_A S$

Table IV

	Excitation kcal/mole	Absorption Max. (Å)
Calc'd for = 0°	87 ± 4	3250 ± 150
Found in 1,2-dithiolane	86	3300
Found in normal disulfides	113	2500

While no calculation has been done for Se compounds, UV absorption measurements do indicate the same sort of red shift going from a non-cyclic diselenide to a cyclic diselenide[19]. For example diethyldiselenide has λmax. at 3115Å whereas the six-membered cyclic compound, 1,2-diselenane has λmax. at 3650Å.



This molecular complex of iodine and tetrahydroselenophene deserves special attention for various reasons. Although recent x-ray crystal determination confirmed it to be definitely of the molecular complex type involving Se·I-I bonding, numerical data at the same time indicate that the structure is tending toward the axial X-Se-X bonding found in R_2SeBr_2 and R_2SeCl_2 compounds[9]. Fig. II gives a view of the molecule along the axis perpendicular to the plane of $C_{(4)}$-$Se_{(3)}$-$C_{(4)}$ and Fig. III gives a view of part of the structure of $C_4H_8Se \cdot I_2$.

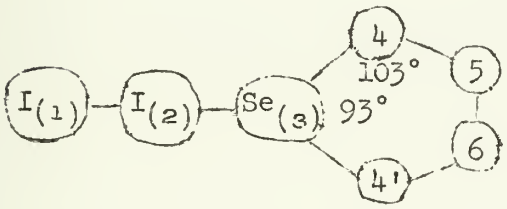


Fig. II

View along axis ⊥ to plane $C_{(4)}$-$Se_{(3)}$-$C_{(4')}$

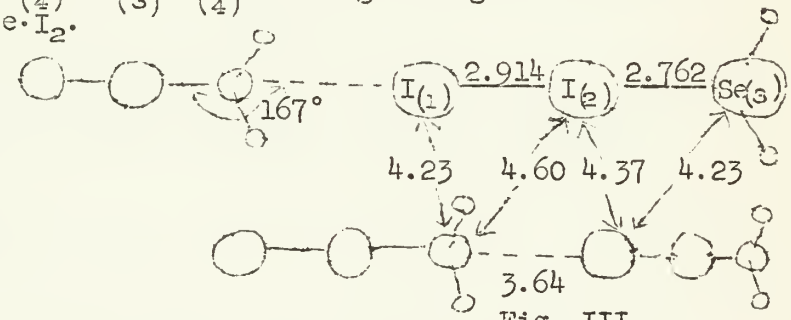


Fig. III

View of part of the structure of $C_4H_8Se \cdot I_2$. $C_{(5)}$, $C_{(6)}$ are not shown

As indicated, this tendency is exhibited through bond lengths and bond angles:

1) short Se·I bond of 2.762Å
2) long I-I bond of 2.914Å
3) short intermolecular contact between $Se_{(3)}$ and $I_{(1)}$ of a neighboring molecule - 3.64Å
4) $I_{(2)}$-$Se_{(3)}$-$I_{(1)}$ angle is close to a straight angle - 167°.

More interesting still is the fact that a four-bond tellurium compound, $(p\text{-}ClC_6H_4)_2TeI_2$ had previously been found to tend toward a molecular complex type bonding[20].

It must be mentioned that while experimental results agree satisfactorily with calculated x-ray data, an assumption had been made that there is a two-fold disorder of the two carbons opposite the selenium atom in the five-membered ring. To obtain more conclusive evidence about the nature of this disorder, Pedersen[21], using wide-line proton magnetic resonance technique,

has found that the molecule is oscillating between two equivalent conformations with a thermally activated motion which is slower than 10 kc sec^{-1} [22] below -140°C and faster than this above -70°C. This is in agreement with Hope and McCullough's suggestion that while the puckering of the ring is equally probable in either of two ways, for symmetry reasons, the packing contacts of the atoms are not changed in going from one configuration to the other and there is no apparent barrier to prevent such interchange of the two forms.

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COMPLEXES OF TRIORGANOTIN HALIDES

T. F. Bolles January 11, 1966

Introduction

Prior to 1960, relatively few complexes of organotin compounds had been reported[1]. Among these, the 1:1 adducts of triorganotin halides with NH_3, pyridine and aniline were of special interest, since they suggested the presence of five-coordinate tin. Since this time, the coordination chemistry of triorganotin compounds has been the subject of much attention[2].

Structure of the Adducts

The infrared spectrum of $(CH_3)_3SnCl\cdot Py$ is consistent with a structure in which the methyl groups are planar[3]. In the solid state, an x-ray study has shown that the molecule is trigonal bipyramidal with the pyridine molecule and chlorine atom lying on either side of a plane including the tin and the methyl groups[4]. This is consistent with the structure proposed for 1:1 adducts of trimethyltin chloride with tetramethylene sulfone, dimethylacetamide, and dimethylformamide[5] on the basis of infrared and n.m.r. spectral data.

Adducts which have been formulated as $[(CH_3)_3Sn(B)_2]^+X^-$ (when $X = NO_3^-$ or ClO_4^-) appear to have a five-coordinate structure about the tin atom analogous to that proposed for the 1:1 adducts. However, no evidence has been found for the existence of 2:1 adducts of this type when $X = Cl^-$ [6-9].

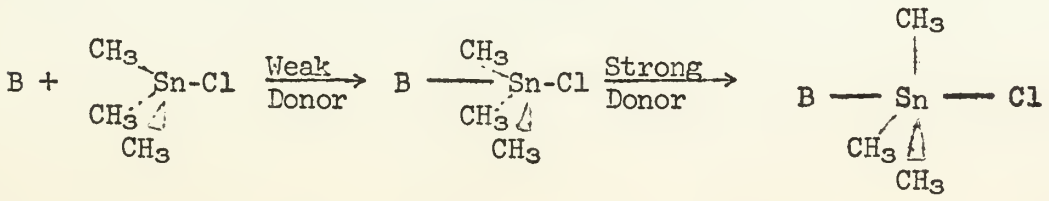
In addition, 1:2 adducts, $B\cdot((C_2H_5)_3SnCl)_2$, are formed with dimethylamine, diethylamine and trimethylamine[10]. The structure of these compounds has not been well established.

Acceptor Properties of Trimethyltin Chloride

In recent work, the equilibrium constant and molar enthalpy of formation of a number of 1:1 complexes of trimethyltin chloride have been measured in non-polar solvents by calorimetric[11], infrared, and n.m.r. procedures. These studies show that trimethyltin chloride interacts more strongly with oxygen and nitrogen donors than with sulfur or phosphorus donors, e.g.,

$$n\text{-}Bu_3P, CH_3C(S)N(CH_3)_2, ((CH_3)_2N)_3PS < C_5H_5N, CH_3C(O)N(CH_3)_2, ((CH_3)_2N)_3PO \quad (1)$$

The magnitude of the tin-proton coupling constant, $J\ Sn^{119}\text{—}CH_3$, of these adducts has been found to be lineally related to the enthalpy of formation of the complex. The changes in $J\ Sn^{119}\text{—}CH_3$ can be interpreted in terms of changes in the s-character the tin employs in the $Sn\text{-}CH_3$ bond, if the Fermi contact term is the dominant coupling mechanism. This change suggests that the trigonal bipyramidal structure of the complex is distorted as illustrated in the following model:



On the basis of this model, steric interactions would be expected, especially for weak donors. The low coupling constants observed for the adducts with Et_2S, Et_2O, pyridine and 2,6-dimethylpyridine support this proposal.

Finally, the proposed double scale equation[12],

$$\Delta H = E_A E_B + C_A C_B \qquad (2)$$

for the prediction of enthalpies of acid-base interactions appears to apply to this system for all cases in which steric effects are not present. In this system, the rehybridization energy must be the same in each case or vary lineally with the magnitude of the donor-acceptor interaction. In situations in which steric effects are present, the calculated enthalpy is much larger than that measured experimentally.

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CIRCULAR DICHROISM AND THE ABSOLUTE CONFIGURATION OF TRANSITION METAL COMPLEXES

John A. Spencer February 8, 1966

I. Introduction

During the past decade both optical rotatory dispersion (ORD) and circular dichroism (CD) have become important tools for the elucidation of absolute configurations of optically active molecules. ORD has been used primarily by organic chemists as a method for relating the structures of many hundreds of complicated natural products. These correlations have been made largely through studies of the vicinal effects of adjacent groups on various chromophores such as carbonyls.[1] From this work has evolved the "Octant Rule" which enables one to predict the sign of the Cotton effect curve for the chromophore given certain information concerning the spacial disposition of vicinal groups.[2] These structural assignments made by means of ORD have been very successful. In view of facts developed in the following pages, however, concerning the greater ease of interpretation, the comparable accuracy of present equipment and other advantages of CD spectra it is surprising to note that comparatively little use of CD has been made by organic chemists.[51]

On the other hand transition metal chemists seeking means of stereochemical correlation are using CD measurements quite extensively. Perhaps this stems from the historic work of Mathieu in the 30's.[3] He recognized the direct value and simplicity of CD spectra. Mathieu's measurements were done by hand using fully optical methods and were at best tedious. Not until the late 50's, a time when ORD equipment was firmly entrenched in the organic laboratory, did a commercial CD instrument, the Jouan Dichrographe, become available. Since the introduction of the Dichrographe it has been widely used by inorganic chemists for structural correlations.[4,5]

It will be the purpose of this seminar to discuss some of the current methods and theories being employed toward the resolution of stereochemical configurations in complexes. It should be noted at the outset that, although the problem of forming a theoretical model for high symmetry transition metal chelates superficially seems to be a relatively simple though laborious task, no single model as yet has been able to account rigorously for the observed phenomena. No rule analogous to the "octant rule" exists. Thus the type of widespread generalization desired for future work in the field can not be permitted at present.

II. Physical Optical Theory of ORD and CD

The earliest observations of optical activity was made by Biot in 1812 when he noticed that the plane of linearly polarized light was rotated after passage through a length of quartz crystal. Thirteen years later Fresnel proposed a physical optical model which with proper interpretation can very satisfactorily demonstrate the relation between ORD and CD. As we shall see it is possible to extend this model to consider the microscopic medium and hence relate molecular structure to optical activity.

We begin by considering an alternate description of a plane polarized beam of light in a field free vacuum. According to Fresnel this can be visualized as two coincident circularly polarized beams each with half the

intensity of the parent plane polarized beam. Restating this the plane polarized beam can be looked upon as the vector sum of the two circularly polarized components over a period of time. We speak of the two beams as being left and right circularly polarized, i.e. the electric vectors move counterclockwise and clockwise respectively for the two components, right and left, with time development or equivalently, motion along the propagation vector $\vec{k}$. (See Figure 1)

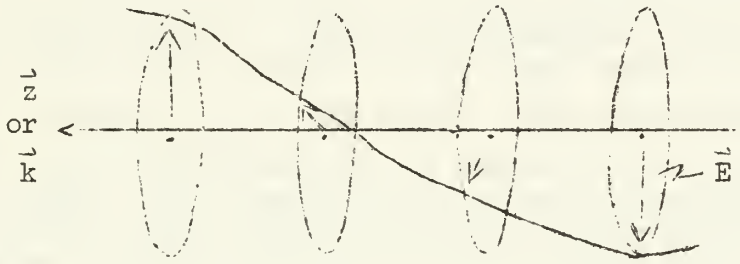


Figure 1. Right Circularly Polarized Light

Looking into the propagation vector and choosing an x,y plane, where both left and right circular components are present we see that the vector sum is just plane polarized light since the electric vectors rotate at the same angular velocity with respect to time development at a point. (See Figure 2)

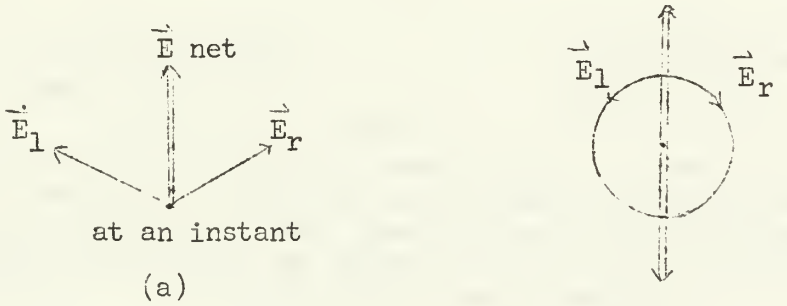


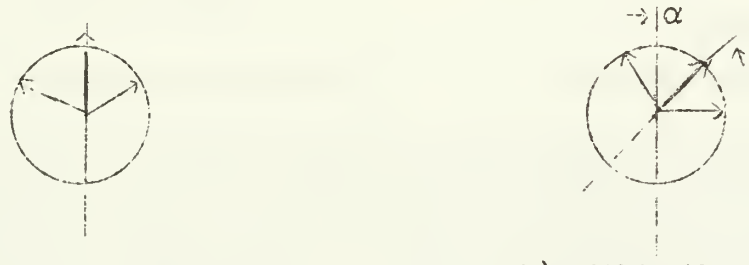
Figure 2

We can characterize the two circular components by two variables: a) the radius relates to the amplitude of the light and b) the degree of helicity looking in three dimensions is equivalent to the wavelength of the light. Thus the model has the properties of the light we wish to describe. Now since the beam is propagating through space the two components must always give unrotated linearly polarized light. This is the same as saying that there can be no phase difference between the two. We will, in the following development, always consider the cross-sectional superposition of the two components, and always examine the resultant waveform. This is in keeping with a polarizer-analyzer experiment where all that can ever be observed is the time average of a superposition of two or more states of polarization.

Consider the consequences of passing a plane polarized beam through two types of media: a) isotropic b) optically active. In the first type the phase difference between the two components remains the same. The index of refraction of the medium is the same for both circular components. Another effect also arises. Namely the intensities or amplitudes of the two components will be reduced. This is represented by a decrease in the radii of the circles in the cross-sectional drawing. Each will be reduced by the

same amount. Looking at the vector sum nothing has changed except the intensity of the plane polarized beam. If one considers that the change in intensity is linearly dependent upon the thickness of the material traversed and the density of particles present, it is easy to see that we have given a physical optical basis for Beer's Law.

Our consideration of optically active media must further be subdivided: 1) far from an optically active absorption band, and 2) at an optically activ band. In the first case it is found that the indices of refraction for the left and right components differ. Define n_l and n_r to be the indices of refraction where $n_l > n_r$. A system with different indices of refraction is known classically as a circularly birefringent medium. Now we know that $n = \frac{\lambda \text{ vac.}}{\lambda \text{ med.}}$. Hence $\lambda_r > \lambda_l$ in the medium. This means that as we progress along the propagation vector into the medium, the two circular components get out of phase. The superposition of the two components at a point in the medium will always give linearly polarized light but rotated at some angle α with respect to the polarization of the incident beam. (See Figure 3)



a) at the interface phase diff. $\varphi = 0$

b) within the medium phase $\varphi > 0$

Figure 3

This angle α is just the optical rotation which we measure in an ORD experiment. It is easily seen that the angle α grows larger as we increase the thickness of material since the phase difference, φ, increases with path length. This relationship was proposed by Biot when he first discovered optical activity. He stated the empirical relation:

$\alpha \propto$ l.d.p
l = path length
d = density of medium
p = weight fraction of optically active material present

The proportionality constant here is just the specific rotatory power $[\alpha]$ with which we are familiar. Note that because the difference in n_l and n_r is not a constant function of wavelength $[\alpha]$ must be specified at a particular wavelength or a suitable plot given i.e. an ORD spectrum.

In the second case we are near an electronic absorption band of the optically active material. We specify that this band be a special type, namely that it comes from an "optically active" transition. We will defer a microscopic definition of this until later. Generally not all bands in the absorption spectrum of a material are optically active. If a band is not active then its ORD is just that of the first case above. In an optically active band we must consider the net of two effects. Both the indices of refraction and the absorption coefficients for left and right circularly polarized light vary as we scan past. (See Figure 4) As before the amount of absorption is represented by a reduction of the amplitude of the circular components. Since $\epsilon_l \neq \epsilon_r$ they differ in amplitude after a small increment

of the material is traversed. It may be demonstrated that if $n_l > n_r$ then ϵ_l must exceed ϵ_r.[9] In the Fresnel model this is represented by a diagram as in Figure 5. The two components never totally extinguish each other.

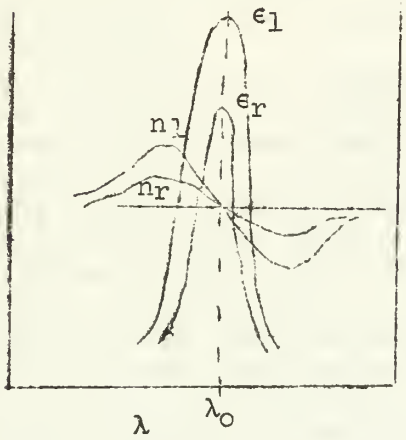


Figure 4. λ_o = center of transition

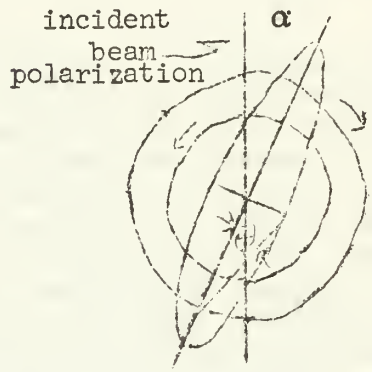


Figure 5

Elliptically polarized light

The resultant electric vector therefore can be seen to trace out an elliptica. path with time, i.e. this is what is termed elliptically polarized light. Notice that the angle of the major axis of the ellipse is at angle α, just the same angle as it would be if no ellipticity occurred. We can now define a new variable θ which describes the ellipticity of the beam of light (see Figure 5). The tan θ is taken to be the ratio of the ~~major~~ minor to ~~minor~~ major axes of the ellipse. Experimentally ellipticities are relatively small so tan $\theta \sim \theta$. It may then be shown that

$$\theta = 0.756 \cdot l \cdot c \cdot (\epsilon_l - \epsilon_r)$$

where l = path length
c = concentration
$\epsilon_{l,r}$ = absorption coefficients.

We see that the ellipticity is directly related to the differential absorption of left and right circularly polarized light. Figure 6 shows a typical plot of α and $\epsilon_l - \epsilon_r$ for an optically active absorption band.

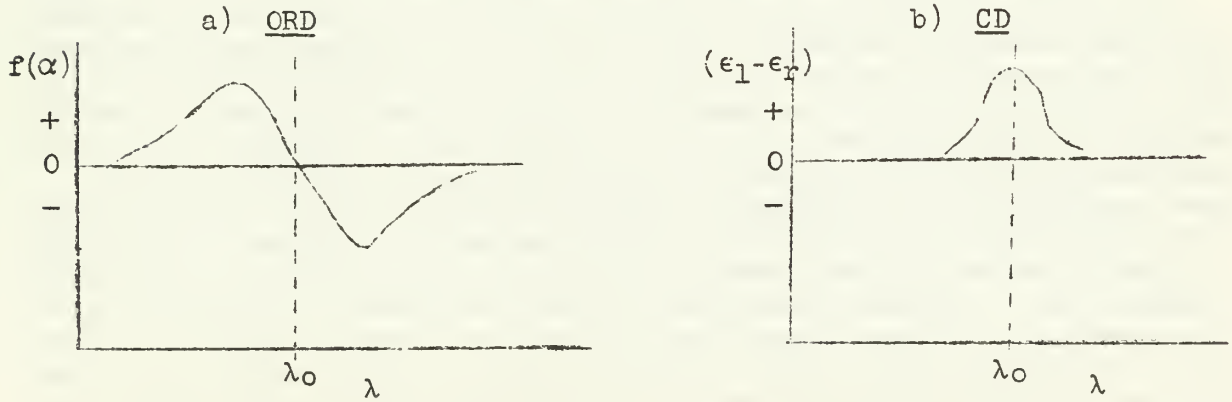


Figure 6. Typical ORD and CD Curves for band at λ_o

We are now in a position to understand the relation between ORD and CD. ORD measures the dispersion of the angle of rotation, α; whereas CD measures the dispersion of the ellipticity near an absorption band. Figure 6 shows what is known as a positive Cotton effect curve. This is one where α goes positive then negative with increasing frequency. The corresponding CD curve has its maximum (for + Cotton effect) at the same point the ORD curve goes through zero. For a negative Cotton effect $\epsilon_l - \epsilon_r$ would take on only negative values.

At this point it is worthwhile to make some brief comparisons between ORD and CD spectra. Of course we recognize that both are experimental measurements of the same phenomenon, viz. molecular electronic transitions. We are not limited to the visible region of the spectrum however. Liehr has suggested that strong optically active bands may be observable in the far infrared and microwave regions as well.[6] The problem is to decide which method gives "better" data. The answer lies in comparison of the ORD and CD line shapes. The ORD anomalous curve has long tails (Drude tails) on each side which extend many thousands of wave numbers away from the center of the band. Indeed when one observes $[\alpha]$ at the sodium D-line he is generally looking at one of the residual tails from a distant Cotton effect curve. This means that where two or more optically active bands are in close proximity one must be careful to subtract out the Drude tails for all the adjacent bands before anything meaningful can be obtained from the band in question. Such a process is arduous and inherently inaccurate where weak bands are concerned (as for the d-d bands in metal complexes). Furthermore the shape of the ORD curve itself is not the type to which we are accustomed in other sorts of experimental data. Thus rapid interpretation of ORD curves to the inexperienced eye is practically impossible. On the other hand in CD spectra the line closes on zero in a relatively small distance on either side of the transition frequency. The residual tails are unimportant except for very closely spaced lines. Because of the shape of CD lines, resolution of absorption band components becomes much easier. In addition, the line shape itself is very close to Gaussian making mathematical analysis more accurate.[7,50] For the novice it is very easy to see immediately the optically active bands and the signs of their respective Cotton effects directly from the chart recorder output.

III. Instrumental Systems for Circular Dichroism

Until the 50's CD measurements as made By Mathieu and others were done by hand, a point at a time. In general the measurement was made of ellipticity θ, directly. Such systems though slow and tedious employ very precise optical equipment and are capable of giving ellipticities of exceedingly high accuracy.[52] As yet no fully automated instrument employing purely optical techniques has been developed. The main disadvantage to the inorganic chemist of using such an instrument is that most optically active materials of interest will racemize by the time the experiment is completed.

The instrument in use today in most laboratories is the Roussel-Jouan Dichrographe. Instead of measuring the ellipticity of the light beam emanating from the sample, it measures directly the differential extinction coefficients $(\epsilon_l - \epsilon_r)$ or $\Delta\epsilon$. To do this it makes use of a unique property of single crystals of deuterated ammonium dihydrogen phosphate. When properly orientated with respect to a plane polarized monochromatic light beam and when an electrical field of a few thousand volts is imposed parallel to the beam, only left or right circularly polarized light (depending on the polarity of the field) is passed by the crystal. This optic element is termed an electro-optic modulation (E-OM) and is the core of the Jouan Dichrographe.

Measurements are made directly by imposing an a.c. field at some frequency (usually 60 c.p.s.) on the E-OM and comparing the photomultiplier detector signal at the positive and negative peaks of the a.c. signal. The CD is then just the value of the a.c. modulation of the detector output. A general schematic is presented in Figure 7.

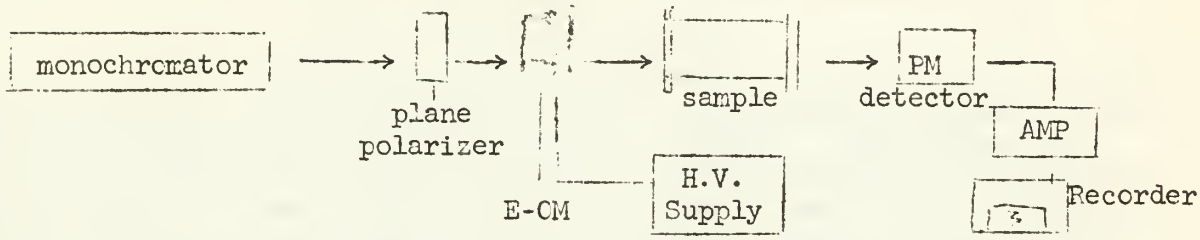


Figure 7. Diagram of Jouan Dichrographe

At present the resolution of CD instruments of this type rivals that of equivalent ORD instruments. The major limitation to higher sensitivity in both cases is the signal to noise ratio.[8]

IV. General Theoretical Models of Optical Activity

The earliest suggestion of a correlation of optical activity with molecular geometry was by Pasteur around 1850. Beginning with the simple fact that left and right handed helices are not superimposable he proposed that optically active crystals had helical elements in their microstructure. He further realized that a tetrahedron with all four apices differing was non-superimposable and hence could also be a source of optical activity. Remember that at this time the internal structure of molecules was not known. Thus Pasteur's idea was quite acceptable for explaining why solid quartz was optically active. But it had been shown that certain liquids and solutions could also be made to rotate polarized light. For many years this was a dilemma since solutions were always thought to be isotropic. Not until the principles regarding internal structure of molecules were developed could the optical activity of solutions be understood.

Today we can see that two possible sources of optical activity can arise. In the case of solids this could be the presence of a non-superimposable inter-molecular configuration (as with quartz). Or in solutions or liquids the molecules themselves are enantromorphous.

We can most easily formulate the criterion for optical activity by reference to group theory. Note that structures which are non-superimposable are those which contain no improper symmetry elements in their group, i.e. reflections, inversions, and rotation-reflections. This is equivalent to saying the molecule must belong to a pure rotational group, i.e. C_3, D_3, C_2, etc.

With an appreciation of the physical optics involved in optically active media we can consider some of the theories which attempt to explain the effect on a microscopic basis. These fall into two major categories: 1) Classical anharmonic oscillator approaches, 2) Quantum mechanical descriptions. Note that most of these calculations have been directed toward ORD but from the interrelation of the phenomena they must also describe CD.

A. Classical Methods

Around 1900 Drude first attacked the problem with a model consisting of a charged particle (e.g. an electron) constrained to oscillate only in

a helical path.[9] The equation he obtained for α is of the form

$$\alpha = \sum_i \frac{R_i}{\lambda^2 - \lambda_i^2}$$

λ_i = wavelength of a vibration along the helix

R_i = a numerical parameter

where we sum over all the transitions of the system. Drude's equation gives the general shape of the ORD anomaly except at the resonant frequency of the transition where the plot approaches + and − infinity. His treatment is quite good in regions far from the band, and in fact permits calculation of the band center in inaccessible regions from data on the tails.[2] A system such as Drude's is often termed a single-oscillator model. It has been possible to "modernize" Drude's picture by including damping terms on the resonant frequency solution. Such calculations can give very close agreement with experimental data. These damping terms may be directly related to the circular dichroism.[2] The important feature of Drude's work is that it clearly demonstrates that a particle moving in a dissymmetric field gives rise to both an electric and a magnetic moment. Or restating this we could say that a molecule must be capable of sustaining both an electric and magnetic dipole field in order that a particle be dissymmetrically constrained and hence exhibit optically active transitions.[10]

In the 30's Born and Kuhn criticized Drude's formulation on the grounds that it did not properly consider molecular structure. They showed that upon a more rigorous treatment of the Drude equation no optical activity could result from a single particle's motion. They went on to propose the coupled oscillator model where several oscillators are required to interact with one another having the net effect of producing both electric and magnetic dipole in their transitions.[11,12,13] Their equations are formally analogous to Drude's. The "octant rule" used by organic chemists can be given partial justification from this model. It has also been used recently by Mason and McCaffery to account for mixing of charge transfer with d-d absorption bands in complexes.[14]

B. Quantum Mechanical Method

The quantum mechanical treatment of optical activity was first done by Rosenfeld.[15] He considers that optical rotatory power in a molecule is due to electronic transitions which have parallel and anti-parallel electric and magnetic transition moments. A rotational strength is defined for a transition a $\rightarrow$ b as the imaginary part of the scalar product transition matrix elements:

$$R_{ba} = \mathrm{Im}\ \langle a | \vec{P} | b \rangle \langle b | \vec{M} | a \rangle$$

where $|a\rangle$ and $|b\rangle$ = wave functions of the molecular electronic states.

$\vec{P}$ = electric dipole moment operator

$\vec{M}$ = magnetic dipole moment operator

We see immediately that if either of the component matrix elements vanishes no rotational strength exists. The signature of R_{ba} is dependent upon the way the electric and magnetic moments couple. R_{ba} may be measured either from the ORD anomaly or directly from the CD band area for a transition. Expressions for the rotational strengths from CD are:

$$R_{ba} = 22.9 \times 10^{-40} \int \frac{\epsilon_l - \epsilon_r}{\nu} d\nu \quad \text{c.g.s. units}$$

or

$$R_{ba} = 0.245\ (\epsilon_l - \epsilon_r)\ \frac{\Delta\nu_{1/2}}{\nu_0} \quad \text{Biots}$$

where the Biot is a unit of rotational strength suggested by Liehr.[6] (1 Biot = 10^{-40} c.g.s) Actually the rotational strength is not unique to the quantum mechanical theory. For example the constant R_i in Drude's equation may be related to R_{ba}.

A result obtainable from both classical and quantum theories which has been used on several occasions states that[16]

$$\sum_{\text{all transitions}} R_{ba} = 0$$

This often holds for the transitions within a particular subgroup of all molecular transitions. Its application has been in evaluating the degree of overlap between adjacent CD bands.

The sign of the Cotton effect for a particular transition is determined by the sign of the rotational strength R_{ba}. Because of the difficulty of setting up accurate molecular wave functions for anything but the simplest systems, present theoretical calculations are limited as to accuracy in predicting rotational strengths. However if simplified models can be made to successfully predict the proper sign of R_{ba} we can be somewhat more confident regarding the physical pictures they evoke.

V. Objectives of Circular Dichroism Studies

Studies of the optical activity and in particular the CD of substances are of value both theoretically and practically. On the theoretical side we wish first to get a better understanding of the nature of the interaction between light and the molecule by which ORD and CD arise. Second we would like to accurately describe the wavelength dispersion of CD and its interrelation with other optical phenomena. Third we would like to be able to predict the rotational strengths of a given molecule under a given experimental situation and especially its sign as related to the absolute configuration of the molecule.

In a more practical vein we wish to be able to accurately resolve and assign absorption band components which are not clearly visible in the ordinary spectra. CD is quite useful here where a molecule is optically active. This is due to the more stringent selection rules involved in optically active transitions (i.e. must be both electrically and magnetically allowed). Thus if one looks at the absorption spectrum of $Coen_3^{3+}$ in solution a single wide band appears in the region 4000Å → 5500Å. This corresponds to the $^1A_{1g} \rightarrow {}^1T_{1g}$ band of the parent octahedral complex $Co(NH_3)_6^{3+}$. From the lower symmetry of the compound (D_3) we know that it must give rise to two transitions: $^1A_{1g} \rightarrow {}^1A_2$ and $^1A_1 \rightarrow {}^1E_a$. In the CD the two bands turn out to have opposite rotational strengths and appear quite plainly (see Figure 8).

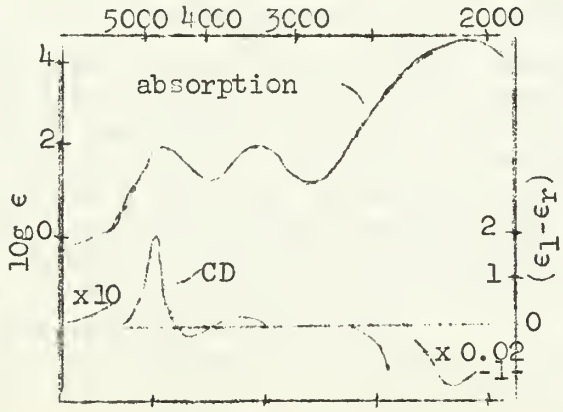


Figure 8. CD and Absorption Spectrum of $Coen_3^{3+}$ [4]

Actually the problem is not solved at this point since we do not know which band is identified with which transition. However we can estimate such things as the absolute values of the field splitting parameters. Band assignments must be made by either calculations of rotational strengths from first principles or other experimental techniques such as polarized crystal spectra.

A second and presently the most intense area of research using CD is in the assignment of absolute stereochemical configurations to molecules. This is done simply by relating the CD spectra of unknown compounds to those of known ones with very similar gross structural features. This will be discussed in considerably more detail in the pages to follow.

A third practical objective of CD measurements is to provide an alternate method for studying such solution effects as the change in degree of chelation with solvents and the formation of outer-sphere coordination complexes. The observation of outer sphere coordination in trigonal complexes by CD is relatively recent. Smith and Douglas reported a remarkable CD band shape change when $PO_4^{\equiv}$ ion was added to $Coen_3^{3+}$ solutions[17]. This was subsequently explained by Mason and Norman as resulting from 1:1 outer sphere coordination by tetrahedral polarizable anions on the C_3 axis of the complex. They supported their assignment with an argument based on the effects of the new ligand on the existing band structure and on the appearance of a new charge transfer band. Further, there was no evidence of complexation for the ion (−) $[Co(+pn)_3]^{3+}$ which is known to be of the <u>ob</u>-form and therefore incapable of ion pairing.[18,19,20]

Yet another application of CD has been in the calculation of "g-factors" or assymmetry factors for various absorption bands. It has been shown that for a transition:[21,22]

$$g = \frac{(\epsilon_l - \epsilon_r)\max \ \Delta\nu_{CD}}{\epsilon \max \ \Delta\nu_{abs.}} = \frac{4R_{ba}}{D_{ba}}$$

where D_{ba} = dipole strength of the absorption; other symbols are as usual.

For a spin allowed transition in an optically active molecule three possibilities exist depending on the allowance. These are

a) allowed electric dipole
   $g \cong 0.01$ with large oscillator strength

b) allowed magnetic dipole
   $g > 0.01$ with a low oscillator strength. The g-value is dependent upon "borrowing" of intensity from other symmetry permitting transitions.

c) both electric and magnetic dipole forbidden
   $g \leq 0.01$ with low oscillator strength.

By calculating these g values and the oscillator strengths for various bands it is possible to find the selection rules and decide on the degree of magnetic allowance. Mason has defined a partial g-factor (g') which has a value at any point along the spectrum[23]. By tracing the change of the g' factor through a composite CD band where the selection rules of the components differ Gillard and coworkers have been able to separate band structures in a number of compounds[24,25]. McCaffery and Mason have applied this method to try to estimate the degree of overlap cancellation between the two magnetically allowed CD bands under the $^4T_{2g}$ of Cr III[26].

A final objective of CD studies is to learn the extent to which vibrational modes, solvent cage effects and charge transfer mixing bear on the CD band shapes. The first of these has been tackled by Moffett and Moscowitz[27].

They propose on theoretical grounds that the vibronic mechanism is considerably less important in CD spectra than in normal absorption spectra. Support for this is witnessed by the smaller half widths of CD bands. At present little is known of the specific solvent effects on CD spectra in solution. Except where ion pairing is possible they are generally consided to be small[27]. Charge transfer mixing as a source of rotational strength has generally been discounted by most authors. However McCaffery and Mason have given a detailed account of how this could be an important source of rotational strength to the d-electron chromophores of complexes[14].

VI. CD Studies of Transition Metal Complexes

In order to develop a coherent theory of optical activity, systems must be studied which are simple enough that they may be properly translated into mathematical language yet general enough that obvious extensions can be made to more difficult cases. Two general types of compounds answer this call. These are: 1) regular helical macromolecules such as proteins and 2) high symmetry transition metal complexes particularly of the trigonal variety. Woldbye has recently summarized the reasons why transition metal complexes are particularly ideal[5].

A. Sources of Optical Activity in Trigonal Complexes

We begin our discussion with trigonal complexes. Two sources of optical activity are present in chelates with puckered rings. The first is the overall D_3 symmetry of the molecule itself. The chromophore with which we are concerned is of course the d-electron system of the metal ion. By group theory we can decide how D_3 field splits the strong field terms for the corresponding octahedral d^n configuration complex. As a specific example consider Co III which is d^6. Figure 9 shows the splitting of the $^1A_{1g} \longleftarrow {}^1T_{1g}$ (O_h) states in the D_3 field.

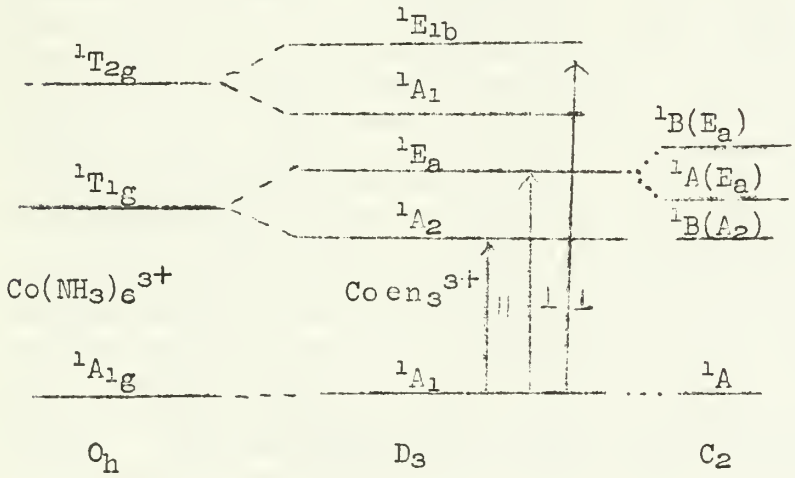


Figure 9

D_3 splittings for strong field d^6 terms. Transition polarization relative to the C_3 axis.

We expect two transitions to appear under the $^1T_{1g}$ band of $Co(NH_3)_6^{3+}$ when we reduce to $Coen_3^{3+}$. We must next decide on the polarizations of the transitions with respect to the symmetry elements of the molecule. This may be done by group theory via reduction of the direct product representation of the ground and excited state. The representation A_2 in D_3 is for parallel components of the electric and magnetic moment vector and E is for the perpendicular components with respect to the C_3 axis[28]. Since the

two bands under $^1T_{1g}$ (O_h) are perpendicular and parallel (see Figure 9) it may be concluded on the basis of a simple helical oscillator model that the two well give rise to opposite rotational strengths. The actual signs of the components will depend on the handedness of the helix about the C_3 axis. Unfortunately many different systems of notation for specification of absolute configurations of molecules are currently being used. The two most applicable are those proposed by Piper[29] and Mason[30]. The molecule in Figure 10 (a) is Δ by Piper's notation and $M(C_3)$ by Mason's. Mason's notation

Δ or $M(C_3)$ (a)

Figure 10

$P(C_2) = M(C_3)$ (b)

has the added flexibility of being able to specify the handedness P or M (positive or negative) of the helical configuration about any rotation axis in the system. Thus in trigonal complexes the specification $M(C_3)$ implies $P(C_2)$ perpendicular to the C_3 axis. In lower symmetry complexes where only a C_2 exists the helical handedness is specified by Mason's notation. It is noteworthy that the sign of the chirality about the C_2 axis in D_3 and C_2 complexes is the same as the sign of the Cotton effect on the E band which usually dominates their rotational strength.

The second source of optical activity in a chelate is related to the conformations of the rings themselves. This constitutes a vicinal effect on the chromophore. The importance of this effect on the chromophore is presently not known. Experimentally it presents a difficult problem in that ions such as trans-$[Coen_2Cl_2]^+$ though capable of having d, l and meso forms undergo much too rapid racemization[5]. Such ions would be ideal since only the ring vicinal effect would give rise to optical activity. If a ligand with a substituent e.g. (d- or l-propylenediamine) is used an additional vicinal effect due to the new independent asymmetric center will occur to complicate the observation. This new vicinal effect could be of considerable importance on the chromophore judging from its usual effect in organic ring systems. Studies of complexes with reasonably planar chelate rings may be of value here. Unfortunately the planarity can not be created by π delocalization because of the lowering in energy of the charge transfer bands such that they mask the d-electron transitions. In fact the tables have been turned in the study of 1,10-phenanthroline and 2,2'bipyridyl complexes where a very high degree of π delocalization occurs. Here assignments have been made by considering the vicinal effect of the d-electron chromophore on the ligand bands[31,32].

B. Stereochemical Induction by Circular Dichroism

1. The Method

At present no rigorous model of the optical activity in trigonal complexes is available. Stereochemical correlations must be made on an empirical basis. To do this we chose a typical compound for which the structure is known. Alas, only one such trigonal complex structure has

been determined[33]. This is the salt $2[(+)Co(en)_3Cl_3]\cdot NaCl\cdot 6H_2O$ which is of the $M(C_3)$ or Δ absolute configuration (see Figure 10a). The solution CD spectra is given in Figure 8. The principle of the method is quite simply that compounds with analogous d^n configurations and stereochemical environments should have the same CD spectra. Since only one reference is available we are for the most part limited to d^6 and d^3(Cr III complexes with ligands in the vacinity of ethylenediamine in the spectrochemical series[5,7]. Most of the attention is focused on the A and E bands under the long wavelength absorption in making the assignments. These are the farthest from the charge transfer region and hence are least likely to be effected by subtle ligand changes. Ultimately our concern is to assign the two bands to their proper respective transitions. Once knowing this then the absolute configuration follows immediately, as we have seen. Most of the successful models presently in use tend to support this method as being valid. Furthermore, to the extent to which it has been applied, corroboration from classical solubility methods, active racemate techniques, biological activities, thermodynamic arguments and others have been quite good (with notable exceptions, e.g. 30). McCaffery, Mason and Ballard have been able to correlate the structures of some eighteen d^3 and d^6 complexes[30]. Several other reports of such work have also been presented[34,35,36].

2. Separation of the A and E Bands

It is worthwhile at this point to discuss some of the techniques which are being employed to varify the CD band assignments. This amounts to finding the ordering of the A and E bands (or put still another way the sign of the trigonal splitting parameter). One method of considerable value is to study oriented single crystals by CD[14,37]. Assuming the general features of the crystal structure are isomorphous to that of $Coen_3^{3+}$ salts, then the CD spectrum taken will light propagating along the optic axis will only be that corresponding to the E band. The sign of the Cotton effect then gives the chirality directly. Along the same line low temperature high resolution absorption spectroscopy can be used to make assignments in solid crystals. These are often based on the symmetry selection rules operating on the vibrational progressions in the band envelope[38]. The use of g-factors as pointed out previously is an additional aid p.107. Still another means has been to note the effect of polarizable anions on the band shapes[19]. And a final method has been to consider the net rotational strengths of the composite band. Mason has shown that the E component is usually favored in trigonal complexes[30].

3. Problems with the Reference

The above should not be interpreted to mean that stereochemical correlations are simply a matter of trial and error in the use of various techniques until a definite indication of the origins of the bands appears. It must be recognized that the method is no better than the standard. Certain recent developments have cast some doubt on this picture. Dingle[39] and Wentworth[40] have examined in detail the low temperature absorption spectra of $Coen_3^{3+}$ and $Co(NH_3)_6^{3+}$, respectively, in the solid state. Indications are that the trigonal splitting in $Coen_3^{3+}$ is exceedingly small. If this is indeed the case then there is considerable question about the origin of the two bands observed in the CD spectra. If Dingle is correct one would expect to see nearly complete cancellation

of the two bands which is apparently not the case. The answer to this problem may be in the extent to which vibronic coupling occurs in optical versus CD spectra. There is considerable uncertainly at present as to the relative importance of the vibrations of the ligand framework on the d-d transitions. Both Dingle and Wentworth feel that these are small on the basis of the vibrational progressions appearing in the polarized crystal spectra. Mason and Norman disagree on the basis of CD band shape changes incurred with deuteration of the N-H bond in $Coen_3^{3+}$.[42] If vibrational modes which cover the entire molecule are important then none of the current quantum mechanical models accounts for the optical activity. Another problem stems from the fact that in the solid state $Coen_3^{3+}$ is in the pure lel-form whereas in solution we expect a mixture of the forms. The solution CD (upon which nearly all correlations are based) represents a superposition of the spectra for all four possible forms[41]. Dingle believes that the local C_3 site symmetry of $Coen_3^{3+}$ in solids may be an additional factor to be considered[39]. Still another doubt has been raised as to the ability to compare systems where π bonding is introduced. π bonding appears to cause many inversions of the expected A-E ordering[7]. Bürer has pointed out that ring size also has a definite effect on the ordering of the levels[7]. Thus there is considerable doubt in the validity of extending the method to cover anything but the most analogous systems.

C. Theoretical Models for Optical Activity in Trigonal Complexes

In light of the above criticism the method must be used with considerable reservation. Two things could potentially correct the current problems. One would be to make more crystal structures available. The other possibility is to formulate a reliable model of the electronic structure in such complexes. As already pointed out much more than just structural correlation is to be gained from such attempts. Ultimately each model seeks to calculate from first principles, sensible values of rotational strength on the basis of some detailed account of the dissymmetric molecular structure.

In order to obtain an idea as to the general direction these current models are taking a brief review of each of the important ones is now given. Five distinct types of calculation have been attempted. Each tries to account for the origin of the rotational strength in a slightly different way. In general we can see that this must come from the addition of electric dipole character to the magnetically allowed d-electron chromophore.

The pioneering effort was made in 1956 by Moffitt[28]. He used essentially a crystal field argument where a static field of odd symmetry, in this case the 4p-electron orbitals was mixed with the 3d-orbitals. The rotational strengths were calculated by first order perturbation theory under the D_3 symmetry crystal field. Sugano, however, has since pointed out that such a model is untenable by a group theoretic procedure[43]. Hamer has extended this argument to show that any odd orbital higher state mixing under a purely D_3 crystal field cannot produce first order rotational strength[44].

In a series of papers Piper alleviated this problem by suggesting a distortion of the pure trigonal field to effectively C_3 symmetry where such a first order rotational strength is possible[29,45,46,47]. The distortion was a "trigonal twist" of the entire molecular framework about the C_3 axis. Such a twist suggests immediately a contingent angular contraction or expansion. This method requires several new angular dependent parameters which must be estimated from the $Coen_3^{3+}$ crystal structure. An interesting result is that a Δ complex with ligand-metal-ligand angular expansion

will have a trigonal field splitting and hence a CD spectrum indistinguishable from a Δ complex with angular compression.

Another model has been proposed by Liehr which uses a molecular orbital approach similar to a treatment of $Co(NH_3)_6^{3+}$.[6] The ligand field is distorted from D_3 symmetry by considering the ligand bonding orbitals to be directed slightly off the bonding axis. No distortion of the nuclear framework is necessary. In conjunction with this model he carries out detailed calculations for all cases d^1 through d^9 with and without spin orbital coupling. In this paper Liehr makes many suggestions as to possible systems which may be best structurally correlated, rotational strength dependence for σ and σ, π bonded complexes, the importance of the degree of covalency and amount of hybridization to rotational strength, as well as a host of others.

Shinada has developed another ionic model similar to Piper's[48]. The field distortion, however, is considered to be caused by charge displacements without movement of the nuclear framework.

Finally mention should be made of the approach of McCaffery and Mason[14]. Here a non-quantum mechanical (coupled oscillator) method is used to attribute electric dipole allowance through mixing of the charge transfer and pure ligand bands with the proper symmetry d-orbital bands. Such a model puts considerably more emphasis on the ligand participation than the above quantum mechanical ones do. This approach may be quite valuable in complexes where accessible ligand bands exist.

D. Extensions to Lower Symmetry Complexes

As a final point it is interesting to consider briefly some very recent extensions of the CD method of stereochemical correlation to complexes of lower than trigonal symmetry[49]. Though surely all the above criticisms apply even more crucially to such work, the concepts used may be of future value. Upon decent in symmetry of C_2 all three components of the triply degenerate bands of O_h symmetry become split (see Figure 9). In complexes of C_2 symmetry where the two odd ligands (or one bidentate ligand) are close to the other two chelating ligands in the spectrochemical series (e.g. (+) or (−) $cis[Coen_2(NH_3)_2]^{3+}$) the effective symmetry remains close to D_3. Thus the splitting of the D_3-E band is relatively small. In light of symmetry considerations only one of the three C_2 components, namely the A coming from the E of D_3 (designated A(E)) is stereoconfigurationally dependent. The other two bands (B(E) and B(A)) do not take their rotational strength from the stereosymmetry determining factors in the molecule according to the coupled oscillator theory. Then the symmetry of the molecule may be obtained from the sign of the rotational strength of the A(E) band in the CD spectrum. A series of bisdiamine complexes of C_2 symmetry have been related to the configuration of $(+)Coen_3^{3+}$ by this method. The authors have also proposed a general method for correlation of any C_2 complex on the basis of a continuous variation between D_3 and C_{2v} symmetry.

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INTERACTIONS OF TRANSITION METAL COMPOUNDS WITH ALCOHOLS AND RELATED SOLVENTS

D. J. Darensbourg February 15, 1966

Introduction

In an attempt to reduce the valency of the transition metal in certain complexes of tertiary phosphines and arsines by the method of Malatesta[1] it was found that the complexes of transition metal halides with tertiary phosphines and arsines interact with alcohols and related solvents to give the following types of compounds (examples in parenthesis): (1) solvates ($[RuCl_3(Ph_3P)_2(CH_3OH)]$)[2], (2) alkoxides ($[ReOBr_2(Ph_3P)_2(OCH_2CH_2OCH_3)]$)[3], (3) hydrides ($[IrHCl_2(Ph_3P)_3]$)[4,5,6,7], (4) carbonyls ($[IrCl(CO)(Ph_3P)_3]$)[6,7,8], and (5) hydridocarbonyls ($[OsHCl(CO)(Ph_3P)_3]$)[6,7,9].

It is the intent of this seminar to examine the scope of these interactions and the details by which the compositions of the resulting metal complexes were deduced.

The use of some of these complexes as homogeneous hydrogenation catalysts will also be discussed.

Scope of Reactions

The latter three types of interactions are by far the more common. The reactions by which these products are formed are (1) reduction, leading to the formation of a hydrido complex together with the aldehyde or ketone corresponding to the alcohol; or (2) carbonylation of the metal resulting in the formation of a carbonyl complex and a degraded fragment of the alcohol. Sometimes both reactions occur simultaneously to give the hydridocarbonyl complex.

These are general reactions of tertiary phosphine and arsine complexes of Group VIII metals with the exception of iron, cobalt, and nickel.

Formation of Hydride Complexes

Two approaches have been used in preparing these complexes.

(1) Simply heating the metal salt and ligand with an alcohol

e.g. $$(NH_4)_2IrCl_6 + Ph_3P \xrightarrow[100^\circ C]{\text{aqueous 2-methoxyethanol}} [IrHCl_2(Ph_3P)_3]$$

(2) Heating the halogeno-phosphine metal complex with alcoholic KOH

e.g. $$[IrCl_3(PEt_3)_3] + KOH \xrightarrow{C_2H_5OH} [IrHCl_2(PEt_3)_3]$$

Other compounds which have been prepared are

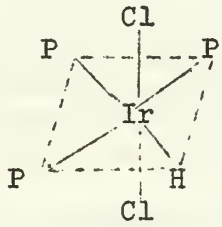
$[IrHCl_2L_3]$, where L = Et_3P[6], Ph_3P, Ph_3As, and Ph_3Sb[4];

$[IrH_2XL_3]$, where L = Ph_3P[4], PEt_2Ph[7] and X = Cl or Br;

and <u>trans</u> - $[PtHCl(PEt_3)_2]$[6].

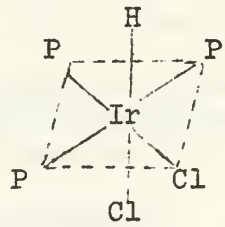
These complexes are diamagnetic, non-electrolytic, and air-stable (with the exception of $[IrHCl_2(PEt_3)_3]$ which is reported to undergo isomerization on standing in air).[6]

Recent infrared and n.m.r. studies by Wilkinson[10] have shown that $[IrHCl_2(Ph_3P)_3]$ which was obtained in the reactions with alcohols to be the α-isomer (I)[11] and the hydride obtained from the reaction of $[IrH_2Cl(Ph_3P)_3]$ and HCl to be the β-isomer (II). These same studies indicate the structure of $[IrH_2Cl(Ph_3P)_3]$ to be consistent with (III).



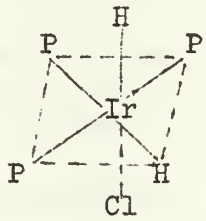
I

α isomer



II

β isomer



III

The principal products from the reactions carried out in ethanol are acetaldehyde and HCl indicating the fate of the ethanol to be

$$CH_3CH_2OH \longrightarrow CH_3CHO + H^+ + H^- \text{ (complex)}.$$

Isotopic studies have shown the hydrogen to originate from the α-carbon when the reaction was run in ethanol.[5]

In addition to primary alcohols, the monohydrides may be obtained with secondary alcohols, ethers, formic acid, and even tert-butanol.

Formation of Carbonyl Complexes

The method of synthesizing the carbonyl complexes is similar to that described for the hydride compounds except higher temperatures and longer reflux periods are required.

e.g. $IrCl_3\cdot(H_2O)_x$ or $(NH_4)_2IrCl_6 + Ph_3P$

$$\xrightarrow[190^\circ C]{\text{aqueous 2-(β-methoxyethoxy)-ethanol}} [IrCl(CO)(Ph_3P)_2]$$

Several of these complexes has been prepared, for example, $[IrX(CO)(Ph_3P)_2]$, where X = Cl or Br[8]; $[RhX(CO)L_2]$, where X = Cl or Br and L = a tertiary phosphine or arsine[6]; and $RuCl_2(CO)_2L_2$, where L = PEt_2Ph or PEt_3[7].

Complexes synthesized using ^{14}C-ethylene glycol as solvent showed the CO ligand to originate from the solvent.

$[IrH_2Cl(Ph_3P)_3]$ has been observed to be a precursor to the carbonyl complex, $[IrCl(CO)(Ph_3P)_2]$[4]. Therefore the possibility exists that the carbonyl complexes result from a reaction with the aldehyde produced by the preceding reaction.

$$RCH_2OH \longrightarrow RCHO + H^+ + H^- \text{ (metal complex)}$$

In fact $[IrCl(CO)(Ph_3P)_2]$ has been obtained from iridium (III) chloride, Ph_3P, and aqueous butanal.[8]

The carbonyl complexes have physical properties similar to those of the hydrides previously mentioned. $[IrX(CO)(Ph_3P)_2]$ reacts with the corresponding halogen hydride to yield the hydridocarbonyl complex.[8]

$$\text{e.g.}\quad Ir^{I}Cl(CO)(Ph_3P)_2 \xrightarrow[\text{ether}]{\text{dry HCl}} Ir^{III}HCl_2(CO)(Ph_3P)_2$$

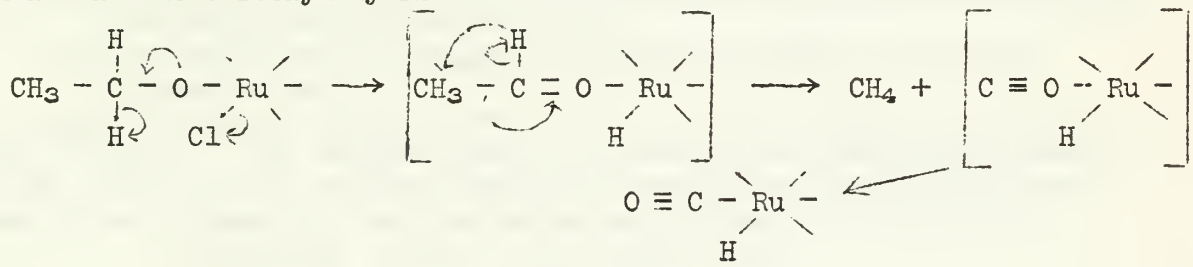
An analogous reaction, with $[PtHCl(Et_3P)_2]$, has been reported, but the product (believed to be $(PEt_3)_2PtH_2Cl_2$) was unstable and not sufficiently characterized.[12] This reaction might be tried with other low valent transition metal complexes in an attempt to synthesize new types of hydrides.

$[IrX(CO)(Ph_3P)_2]$, where X = Cl or Br, has been shown to be isomorphous with $[RhCl(CO)(Ph_3P)_2]$. For the latter, the <u>trans</u> square-planar structure has been confirmed by X-ray studies.[13]

<u>Formation of Hydridocarbonyl Complexes</u>

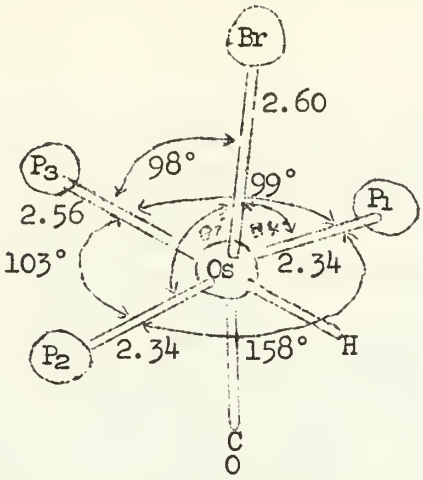
The reaction of hexahalogeno-osmate (IV) or ruthenium trichloride with tertiary phosphines and arsines in the presence of alcohols or ethanolic potassium hydroxide gives the series of hydridocarbonyl complexes of the general form $[Os^{II}HX(CO)L_3]$ and $[Ru^{II}HX(CO)L_3]$, where X = Cl or Br and L = a tertiary phosphine or arsine[6,9]. These compounds were earlier incorrectly formulated as square-planar derivatives of univalent osmium and ruthenium, $[OsXL_3]$ and $[RuXL_3]$[14].

A mechanism has been proposed to explain the formation of the ruthenium complexes (and presumably the osmium reaction takes the same path)[15]. When the reaction is run in ethanol first an ethoxide complex is formed, followed by the transfer of a hydride ion from the α-carbon atom of the ethoxide group to the metal giving an acetaldehyde complex which finally breaks down to methane and the carbonyl hydride.



Methane has been detected as one of the reaction products, and tracer studies with ^{14}C show that the carbonyl group comes from the alcohol.

An X-ray crystal structure has been done on $[OsBrH(CO)(PPh_3)_3]$.[16]



Molecular configuration of $[OsHBr(CO)(PPh_3)_3]$ (bond lengths in Å).

The structure obtained from X-ray evidence is consistent with the magnetic properties of $[OsHBr(CO)(PPh_3)_3]$ (diamagnetic, 76-400°K) and its isostructural analogues $[MHX(CO)L_3]$, where M = Os or Ru, X = Cl or Br and L = PPh_3 or $AsPh_3$.[14b,17] These data along with isotopic and infrared spectral evidence are in agreement with the formulation of the complexes as octahedral compounds of spin-paired d^6_ϵ configuration, eliminating a square-pyramidal structure of an Os(1) species (i.e., without the hydrogen) which might have appeared possible solely on the basis of X-ray data.

Homogeneous Hydrogenation Catalysis

Vaska has shown that square-planar carbonyl complexes of univalent iridium and rhodium, trans-$[MX(CO)(Ph_3P)_2]$ (M = Ir, Rh and X = halogen), are excellent catalysts in reactions of ethylene, propylene, and acetylene with molecular hydrogen[18,19]. $[MH_2X(CO)(Ph_3P)_2]$ is proposed as the catalytic intermediate in these reactions. This system offers many important features not present in previously reported examples of homogeneous catalytic hydrogenations in solutions[20].

(a) The compositions, properties, and structures of the catalyst complexes are known.
(b) The iridium complexes react reversibly with one mole of hydrogen per complex.
(c) The iridium complexes react reversibly with ethylene, acetylene, and other unsaturated substrates.
(d) The intermediate $[IrH_2X(CO)(Ph_3P)_2]$ has been isolated and characterized.

Wilkinson and co-workers have studied a system similar to that of Vaska[20a,20b,21]. The catalyst used by Wilkinson was $(Ph_3P)_3RhX$, where X = Cl, Br, or I. N.m.r. studies indicate a species with metal-to-hydrogen bonds as an intermediate and the mechanism proposed is as follows:

$$(Ph_3P)_3RhCl \rightleftharpoons (Ph_3P)_2RhCl + Ph_3P$$

$$(Ph_3P)_2RhCl(s)_{1\ or\ 3} \xrightleftharpoons{H_2} (Ph_3P)_2RhCl(s)H_2$$

$$(Ph_3P)_2RhCl(s)H_2 \xrightleftharpoons{RC{=}CR'} (Ph_3P)_2RhCl(RC{=}CR')H_2$$

$$(Ph_3P)_2RhCl(RC{=}CR')H_2 \longrightarrow (Ph_3P)_2RhCl(s)_{1\ or\ 3} + RHC{-}CHR'$$

where S = solvent molecule. Much of the details of this mechanism remains to be elucidated.

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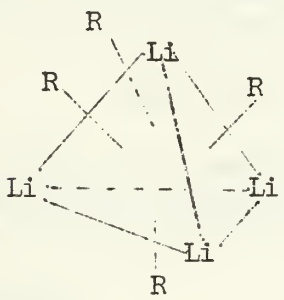
SOME PROPERTIES OF ALKYLLITHIUM COMPOUNDS IN SOLUTION AND IN THE VAPOR STATE

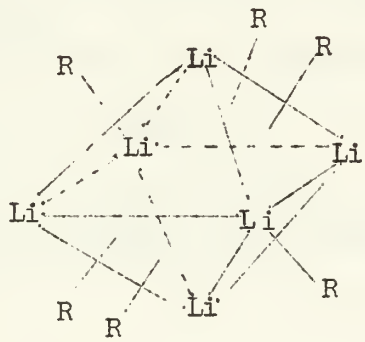
George Hartwell February 22, 1966

Introduction

Alkyllithium compounds have been used for many years, but in order to understand their role in the mechanisms of organolithium reactions it has become increasingly more important to have a knowledge of their structures. Crystal structures for ethyllithium[1] and methyllithium[2] have shown loosely associated tetramers in the solid state, with the alkyl groups bonded to the faces of an inner tetramer of lithium atoms.



Tetramer



Hexamer

Using mass spectrometry, ethyllithium has been shown[3] to consist of a mixture of tetramers and hexamers in the vapor state, and alkyllithium compounds in hydrocarbon solvents have shown mainly four and six fold association,[4,5,6] i.e., ethyllithium—6, t-butyllithium—4, lithiomethyltrimethylsilane—4. A current review discusses the structures of these compounds in more detail.[7]

Li^7 and H^1 NMR

Li^7 NMR of a mixture of ethyllithium and t-butyllithium in benzene gave evidence for mixed associated species.[8] In an effort to learn more about the nature of these polyhedra, a simpler system using tetrameric t-butyllithium (I) and tetrameric lithiomethyltrimethylsilane (II) was investigated in cyclopentane. Their interaction was studied over a wide temperature range using both Li^7 and H^1 NMR. The five expected tetrameric species $Li_4X_{4-n}Y_n$ approached a statistical distribution through slow intermolecular exchange.

The five peaks observed in Li^7 NMR also require a fast intramolecular exchange leading to the equivalence of the four lithium atoms in each

tetramer. However, at temperatures below -25°C the spectrum changes to four peaks, and can be explained using a "local environment" hypothesis where, each lithium now may have an environment of (3X), (2X,Y), (X,2Y), or (3Y).

The same experiment in toluene gave the same four peaks below -25°C, again indicating slow inter- and intramolecular exchange (on the NMR time scale). However, upon increasing the temperature there was a gradual collapse of the peaks on the lithiomethyltrimethylsilane side until at the maximum temperature reached, 91°C, only two remained. Thus it can be concluded that there is an increasingly faster intermolecular exchange until all species except the t-butyl tetramer are rapidly exchanging at 91°C. Proton NMR is also in agreement with these observations.

Mass Spectrometry

A few alkyllithium compounds were also studied in the vapor phase using mass spectrometry, and appearance potentials were determined for lithiomethyltrimethylsilane and lithium t-butoxide. Lithiomethyltrimethylsilane and t-butyllithium are mainly tetrameric, while lithium t-butoxide is hexameric. A mixture of t-butyllithium and ethyllithium isolated from solution yielded mixed tetrameric species.

The ions observed follow the same pattern as for ethyllithium,[3]

$$Li_nR_n + e^- \longrightarrow Li_{n-x}R_{n-x-1}^{+} + R + Li_xR_x + 2e^-$$

the largest mass peaks occurring when x is an even integer. Thus the polyhedra of high stability are hexamers and tetramers, with a much higher energy dimer as the next most stable species.

Conclusion

Using NMR both inter- and intramolecular exchange have been observed in hydrocarbon solvents for alkyllithium compounds. The rate constant for dissociation is on the order of 10^3 times larger in toluene than in cyclopentane, indicating a donor-acceptor interaction between the aromatic solvent and the alkyllithium polyhedron.

Mass spectrometric investigations show agreement between solution and vapor phase association, and give evidence for a high energy dimer.

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OPTICAL ACTIVITY AND ELECTRONIC STRUCTURE OF COORDINATION COMPOUNDS

Richard S. Treptow March 1, 1966

INTRODUCTION

Optical activity has a long tradition of application to chemical problems. Molecular structure, kinetics and mechanisms have been studied by the phenomenon of rotation of plane polarized light. With the quantum mechanical interpretation of this effect given by Rosenfeld[1], optical activity can become a tool for spectroscopic studies into the electronic structure of compounds.

PRINCIPLES

The physical optical theory of ORD (optical rotatory dispersion) and CD (circular dichroism) has been thoroughly reviewed in recent years[2,3,4]. It will suffice here to emphasize the relationships between the two parameters associated with an electronic transition, $a \rightarrow b$, of an optically active chromophore. These parameters are the dipole strength, D_{ba}, and the rotational strength, R_{ba}. Experimentally they are determined by the integrated intensity of the absorption and CD bands respectively.

$$D_{ba} = 91.8 \times 10^{-40} \int \epsilon/\nu \, d\nu \qquad (1)$$

c.g.s. units

$$R_{ba} = 22.9 \times 10^{-40} \int \Delta\epsilon/\nu \, d\nu \qquad (2)$$

c.g.s. units

The quantum mechanical expression for the rotational strength was established by Condon[5].

$$R_{ba} = I_m \langle a / \vec{P} / b \rangle \langle b / \vec{M} / a \rangle \qquad (3)$$

The first of the bracketed quantities is the electric dipole transition moment, and the other is the magnetic dipole transition moment. In an analogous manner we have the expression for the dipole strength.

$$D_{ba} = \langle a / \vec{P} / b \rangle \langle b / \vec{P} / a \rangle \qquad (4)$$

Thus whenever it is possible to place a transition metal ion in an optically active environment its electronic transitions can be examined in ORD or CD as well as in absorption spectroscopy. Equations (1-4) form the basis for the calculations and selection rules used in the applications to be discussed.

APPLICATIONS

Intensity Mechanism of Absorption Spectra. The ligand field transitions of centrosymmetric complexes are Laporte forbidden due to the selection rule

obtained by application of equation (4). Many complexes such as trans-$[Co(l\text{-}pn)_2Cl_2]^+$ are nearly, but not exactly, centrosymmetric. A question arises as to the origin of the absorption intensity. Calculations of Wentworth and Piper[6] from CD data indicate that it is the vibrational, rather than the static, deviation from symmetry which predominates in the dipole strength. McCaffery and Mason[7] have divided the dipole strength of d-$[Co(en)_3]^{3+}$ into a "rotationally active" and "rotationally inactive" portion. The former was used in equation (3) to calculate the magnetic transition moment.

Detection and Identification of Electronic Transitions. The fact that R_{ba} and D_{ba} have different selection rules is of great value in these studies. Recent work in this laboratory illustrates one application.

The optically active chelate levo-trans-1,2-diaminocyclohexane (l-chn) coordinates to a metal ion in a manner analogous to ethylenediamine. The complexes prepared were trans-$[Co(l\text{-}chn)_2X_2]^+$ (where X = F^-, Cl^-, Br^- and NO_2^-), trans-$[Co(l\text{-}chn)_2(NH_3)_2]^{3+}$, and trans-$[Co(l\text{-}chn)_2NH_3Cl]^{2+}$. As is usually the case, circular dichroism curves detect more transitions than either ORD or absorption curves. The CD of trans-$[Co(l\text{-}chn)_2Cl_2]^+$ is shown in Figure 1.

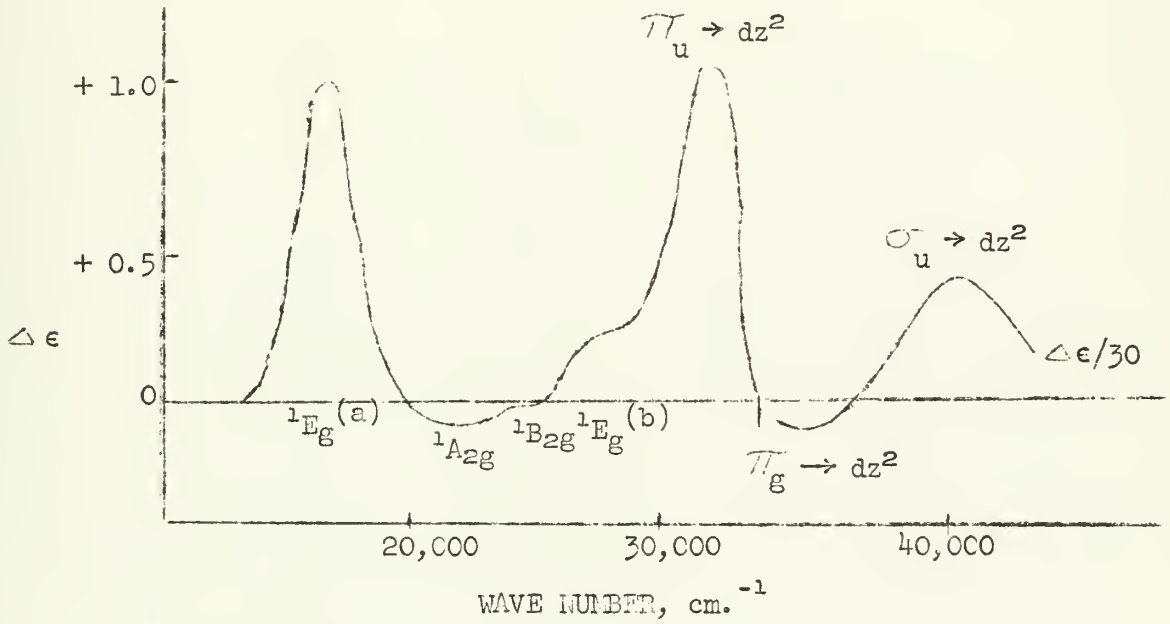

Figure 1. Circular dichroism of trans-$[Co(l\text{-}chn)_2Cl_2]^+$

Notation used to label bands is explained in text.

Although this complex belongs to the D_2 point group, to a good approximation the coordination sphere is tetragonal. The magnetic selection rules of the D_{4h} point group have been used in assigning the ligand field transitions $^1A_{1g} \rightarrow {}^1E_g(a)$, $^1A_{2g}$, $^1B_{2g}$ and $^1E_g(b)$. These excited states are indicated in Figure 1. The assignments of $^1E_g(a)$ and $^1A_{2g}$ are in agreement with those of Ballhausen and Moffit[8] based on the polarized crystal spectrum of trans-$[Co(l\text{-}chn)_2Cl_2]^+$. The $^1B_{2g}$ and $^1E_g(b)$ states have been detected for the first time. The ligand-metal charge transfer transitions have also been assigned.

They are indicated in Figure 1 with one-electron molecular orbital notation[9]. Other workers have made various assignments of these charge transfer transitions on the basis of absorption spectra. Their opinions have been summarized by Yamatera[10].

With the added d-d transitions observed in CD, it has become possible to make a judgment on the two models discussed by Wentworth and Piper for acidoammine cobalt(III) complexes. The crystal field[11] and molecular orbital[12] models make different predictions as to the ordering of the one-electron energy levels of the d-orbitals. Calculations now indicate the MO ordering to be correct. It has also been possible to construct a two-dimensional spectrochemical series as suggested by McClure[13]. The principal factor which determines the position of a ligand in the series is the σ rather than the π - interaction.

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REACTIONS OF COORDINATION COMPOUNDS IN THE SOLID STATE

H. Eugene LeMay March 8, 1966

INTRODUCTION

Though solid-state reactions involving coordination compounds have been known for some time and have often been used in preparative techniques, few of these have been studied in any detail. It would seem that much valuable information concerning reactions and reaction mechanisms of coordination compounds could be gained from a more thorough study of these reactions. There is much information available on the reactions of coordination compounds in solution[1,2,3,4,5] and on the solid-state reactions of other inorganic compounds[6,7,8,9] which could be applied to the problem. Furthermore, many thermoanalytical techniques are available for such a study.[10,11] Unfortunately, there are fewer applicable experimental parameters available for investigation in the solid state than in solution, and such extraneous factors as particle-size and lattice defects are often of considerable importance.

It is the purpose of this seminar to review the types of solid-state reactions which are known to involve coordination compounds of the transition metals. In this regard, there are certainly many brief, published accounts of reactions which are not readily found in the literature and hence not mentioned in this seminar. Furthermore, only reactions of the type A $\rightarrow$ products will be discussed even though some reactions of the type A + B $\rightarrow$ products have been reported.

GENERAL CHARACTERISTICS OF SOLID-STATE REACTIONS

Before discussing the reported solid-state reactions, it is best to discuss some of the general characteristics of such reactions. Reactions in the gaseous state and in solution take place at a uniform rate throughout the reaction zone; the reacting system is independent of space coordinates and is hence described by equations involving only time and reactant concentrations. In the solid state, however, reactions are dependent also on space coordinates. In principle at least, the reactions can be described in terms of a movement of interphase boundaries. This leads to kinetic expressions resembling those for diffusion controlled reactions. Thus, in the case of solid-state reactions, we must concern ourselves not only with the chemical change itself but also with the formation and movement of interphase boundaries. These latter two processes are referred to as nucleus formation and growth.

Solid-state reactions are generally described by relating the extent of reaction, α = (amount reacted)/(amount of initial reactant), with time. A plot of α versus time often shows reactions to occur in three steps, 1) induction or initiation, 2) growth, and 3) decay. Frequently encountered kinetic expressions for the growth stage of a solid-state reaction are $\alpha = Ct^n$, $\alpha = Ce^{kt}$, $\log(\alpha/1-\alpha) = kt + c$, and $-\log(1-\alpha) = kt$. It is possible to derive the last expression by assuming that nucleation on a spherical particle is random and that the reaction proceeds from the nucleated surface towards the interior by a contracting-sphere movement of the interface[6].

REPORTED SOLID-STATE REACTIONS

I. Linkage Isomerism:

Perhaps the most familiar solid-state reactions known to involve coordination compounds are the nitrito-nitro isomerizations. Isomerization of this type is noted to occur in many cobalt(III) complexes and in the pentammines of rhodium(III), iridium(III), and platinum(IV)[12,13,14]. With the single known exception of trans-$[Co(py)_2(NH_3)_2(ONO)_2]SCN$[15], all reactions which occur in solution also occur in the solid state. This suggests that little or no change occurs in the crystal lattice during the reaction. The compounds $[Co(NH_3)_5NO_2]Cl_2$ and $[Co(NH_3)_5ONO]Cl$ have been shown to be isomorphous (this led some investigators to conclude that these were the same compound even though the first is yellow and the second red, and though they exhibit different IR spectra)[16]. Furthermore, this isomerism has been shown to be reversible in the cases of $[Co(NH_3)_5NO_2]X_2$, where X = Cl, Br, I, and NO_3[17], and $[Ir(NH_3)_5NO_2]Cl$[14], the reverse reaction being induced by ultraviolet radiation.

Linkage isomerism involving SCN^- and CN^- has also been reported to occur in the solid state. Burmeister and Basolo have found $[Pd(bipy)(SCN)_2]$ and $[Pd(As\varphi_3)_2(SCN)_2]$ to change from S-bonded to N-bonded in the solid state[18]. Shriver and his coworkers have reported that $KFeCr(CN)_6$ changes from brick red to dark green when the solid is heated to 100°. The corresponding change in the IR suggests that the initial material contains Cr^{III} - C≡N - Fe^{II} linkages while the product contains Cr^{III} - N≡C - Fe^{II} linkages[19].

II. Racemization:

Several compounds have been found to undergo solid-state racemization under various experimental conditions. Of these, the trisoxalato complexes of chromium(III) and cobalt(III) have received the most attention. Johnson and his coworkers have studied the solid-state racemization of $K_3[Cr(OX)_3]\cdot 2H_2O$,[20] $(stry)_3[Co(OX)_3]\cdot nH_2O$ and $(stry)_3[Cr(OX)_3]\cdot nH_2O$,[21] where stry = strychnine and OX = oxalate. Since all three of these complexes show somewhat different behavior, no general conclusions as to the racemization process can be drawn. Johnson, however, has proposed that water plays an important role in the reactions.

The effect of pressure on the racemization of $K_3[Co(OX)_3]\cdot 2\text{-}3H_2O$ has also been investigated[22]. Since increasing pressure has an accelerating influence on this racemization, it was suggested that the transition-state in the racemization process is of smaller volume than the initial or final state. The role of the lattice water, however, has not been determined. Furthermore, it has not been shown that the optically active and racemic compounds are of the same crystal structure. This latter must be true if the effect of pressure is to be attributed entirely to the racemization and not a combination of racemization and crystal structure changes. Since $[Fe(phen)_3](ClO_4)_3$,[23] where phen = ortho-phenanthroline, undergoes solid-state racemization under pressure while $[Fe(phen)_3]I_3$[24] does not, lattice effects appear to be of importance. Suggestions that one of the oxalate ligands may not be functioning as a bidentate ligand in the salts of $Cr(OX)_3^{3-}$ and $Co(OX)_3^{3-}$ are also noteworthy in connection with the solid-state racemization of these compounds.[25,26]

Many other compounds apparently racemize in the solid state. The tristhiooxalato complex of cobalt(III) undergoes a rapid loss of optical activity at room temperature, but this may be partially due to decomposition.[27] Even

such a usually inert complex as $[Co(en)_3]I_3 \cdot H_2O$ has been noted to undergo racemization when heated in the solid state.[28] It has been suggested that this process is related to the lattice water present, but racemization proceeds long after this water has been driven off. Furthermore, such racemization also occurs for $[Co(en)_3](NCS)_3$ which contains no lattice water.[29]

The compounds cis-$[Cr(en)_2Cl_2]Cl \cdot H_2O$, cis-$[Co(en)_2Cl_2]Cl \cdot H_2O$, and cis-$[Co(en)_2(H_2O)Cl]Cl_2$ also racemize when heated in the solid state. In the first compound, racemization appears to be related to the loss of water of hydration.[29]

III. Thermal Decompositions:

Perhaps the largest class of solid-state reactions involving coordination compounds are the thermal decomposition reactions. Of these, the reactions involving removal of a volatile ligand from the coordination sphere are perhaps the most interesting and have received the most attention. Rather than list all the compounds that react in this fashion, only those which have been investigated in some detail in more recent literature will be mentioned. Standard works such as Gmelin's "Handbuch der Chemie" and Pascal's "Noveau Traite de Chimie Minerale" should be consulted for further examples.

Reactions of the type

$$[Co(NH_3)_5(H_2O)]X_3 \xrightarrow{\Delta} [Co(NH_3)_5X]X_2 + H_2O$$

$$[Co(NH_3)_4(H_2O)_2]X_3 \xrightarrow{\Delta} [Co(NH_3)_4X_2] + 2H_2O$$

appear to be quite general. The halide complexes have been studied by Wendlandt by use of thermoanalytical methods such as DTA, TGA, and gas-evolution techniques.[30,31] The only known exceptions to these reactions are the perchlorates[32]. It has been argued on the basis of these exceptions that these dehydration (or anation) reactions are S_N2 and hence dependent on the coordinating ability of the anion in addition to the volatility of the coordinated water.[33] However, such a conclusion is based on arguments which completely ignore the effect lattice changes have on whether or not a reaction will occur.

Ammonia is readily lost from many complexes[34,35] as is pyridine.[36] The cobalt(III) complexes $[Co(NH_3)_6](NO_2)_3$, $[Co(NH_3)_5NO_2](NO_2)_2$,[37] cis and trans-$[Co(NH_3)_4(NO_2)_2]NO_2$,[37] cis and trans-$[Co(en)_2(NH_3)_2](NO_2)_3$[38] and optically active cis-$[Co(en)_2(NH_3)_2](NO_2)_3$,[39] all lose ammonia upon heating to form well defined intermediates. Perhaps one of the most interesting results of these reactions and the dehydration reactions is the stereospecificity which they exhibit. Thus both cis and trans-$[Co(en)_2(NH_3)_2](NO_2)_3$ yield cis-$[Co(en)_2(NO_2)_2]NO_2$, while cis-$[CoA_4(H_2O)_2]Cl_3$ yields cis-$[CoA_4Cl_2]Cl$ where $A_4 = (NH_3)_4$ or $(en)_2$ (but trans-$[Co(trien)Cl_2]Cl$ is obtained from cis-(α)-$[Co(trien)(H_2O)Cl]Cl_2$,[40] where trien = triethylenetetramine). Similarly, cis-$[Cr(en)_2Cl_2]Cl$ is obtained by heating $[Cr(en)_3]Cl_3$ in the presence of NH_4Cl, but trans-$[Cr(en)_2(SCN)_2]SCN$ is obtained when $[Cr(en)_3](SCN)_3$ is heated with NH_4SCN.[41,42,43]

Other recent studies include the decomposition of oxalato complexes of manganese(III)[44] and cobalt(III)[45], the decompositions of $[M(bipy)_3]Br_2$,[46] where $M = Mn^{+2}$, Fe^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, and Zn^{+2}, and $[Rh(NH_3)_5(H_2O)](ClO_4)_3$.[33] Also of interest is the room temperature dehydration of $[Cu(Sal)_2 \cdot 2H_2O]$, where Sal = salicylate. In this case there is a change from an octahedral, monomeric molecule to a dimer, $[Cu(Sal)_2 \cdot H_2O]_2$ which has Cu - Cu bonds and bridging salicylate groups.[47]

IV. Other Reactions:

The compounds trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$,[48] trans-$[Co(l\text{-}pn)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$,[49] where l-pn = levo-propylenediamine, and trans-$[Ru(Cl)_2(CO)_2(PR_3)_2$,[50] where R = $P(C_2H_5)_2(C_6H_5)$, all reportedly undergo solid-state trans to cis isomerizations. Of these three reactions, only the first has been studied in any detail. It has been found that the rate of water loss and the rate of disappearance of trans-$[Co(NH_3)_4Cl_2]IO_3$ are both first order, and the rates of the two processes are equal over a range of temperatures. Furthermore, the rate of disappearance of trans-$[Co(NH_3)_4Cl_2]IO_3$ is greatly increased under vacuum. When heated in an atmosphere of water vapor, the rate of disappearance of trans-$[Co(NH_3)_4Cl_2]IO_3$ is increased, but this appears to be due (at least in part) to the formation of $[Co(NH_3)_4(H_2O)Cl]Cl \cdot IO_3$. According to TGA data, the two moles of lattice water are lost in a single step, though DTA shows two endothermic transitions in the 90-115° region. As is observed in many other dehydration reactions, the product, cis-$[Co(NH_3)_4Cl_2]IO_3$, is microcrystalline.[29] It is possible that the dehydration process, disrupting the crystal lattice, simply provides the necessary energy for the isomerization to occur intramolecularly.

Nickel(II) compounds have been noted to undergo changes in coordination number and geometry in the solid-state. Both $[NiBr_2\{P(C_2H_5)(C_6H_5)_2\}_2]$ and $[NiBr_2\{P(i\text{-}C_3H_7)(C_6H_5)_2\}]$ reportedly undergo a square planar to tetrahedral change at room temperature.[51] The compound $[(C_6H_5)As]_2[Ni(NCS)_4]$ undergoes a change at 155° from an octahedral (with NCS bridges) to an approximately tetrahedral geometry.[52]

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THE CHEMISTRY OF TETRASULFUR TETRANITRIDE

Christopher W. Allen March 15, 1966

I. Introduction

The chemistry of sulfur-nitrogen compounds is a varied and interesting one, and it has been a topic of interest to the inorganic chemist since the first synthesis of tetrasulfur tetranitride, S_4N_4, in 1835[41].

Any comparisons which one might wish to make with nitrogen-oxygen compounds are totally absent. This may be ascribed to the fact that the nitrogen is the less electronegative partner in binary nitrogen-oxygen compounds (hence nitrogen oxides) whereas nitrogen is the more electronegative partner in binary sulfur-nitrogen compound (hence sulfur nitrides).

The chemistry of sulfur-nitrogen compounds has several general features which are commonly exhibited in their behavior. Some of these characteristics are: stability of the sulfur-nitrogen bond, tendency to form six- and eight-membered rings, ring contraction, polymerization, and negative ion formation.

There are several older reviews available on various aspects of sulfur-nitrogen chemistry[2,5,6,8,10,33,37,53]. In this seminar, I shall consider various aspects of the chemistry of tetrasulfur tetranitride, S_4N_4.

II. Preparation and Properties

A) Preparation

1. Ammonylsis of sulfur halides

   a) $S_2Cl_2 \xrightarrow{NH_3} S_4N_4$ [9]

      i) S_7NH occurs as a by-product, but it may be separated by solvent extraction or by chromatography[70].

   b) $S_2F_{10} \xrightarrow{NH_3} S_4N_4$ [23]

   c) $SF_4 \xrightarrow{NH_3} S_4N_4$ [24]

2. Disproportionation of elemental sulfur in liquid ammonia[5].

   a) $10S + 4NH_3 \rightleftharpoons 6H_2S + S_4N_4$

3. Miscellaneous methods.

   a) $S_2Cl_{2(vapor)} \xrightarrow{NH_4Cl} S_4N_4$ [44]

   b) $S_2Cl_2 + \xrightarrow[0°C.]{LiN_3} S_4N_4$ [38]

   c) Active nitrogen with sulfur compounds.

      i) $[N] \xrightarrow{S_2Cl_2} S_4N_4$ + other products[69]

      ii) $[N] \xrightarrow{S_{2(vapor)}} S_4N_4 + (NS)_x$ [16]

B) Physical Properties

Tetrasulfur tetranitride is an orange-red crystalline solid of the class C_{2h} and space group $P2_1/n$. It melts at 178°C. with decomposition and is soluble in many organic solvents.

It is unstable thermodynamically. It is strongly endothermic with $\Delta H_{formation}$ being equal to $110.0 \pm 2 \frac{K.Cal}{Mole}$ [3]. This is borne out by the fact that it has a tendency to explode when struck. The sulfur-nitrogen bond strength has been estimated to be 73.5 ± 1 K.Cal/Mole on the assumption of only sulfur-nitrogen bonds being present[3].

The dipole moment has been measured to be 0.72 D.[60] Tetrasulfur tetranitride is diamagnetic with a magnetic susceptibility of $X_{mol} = -102 \times 10^{-6}$.[39]

III. Structure

A. Geometrical

The geometrical structure of the S_4N_4 molecule has been a subject of controversy for a long period of time and in fact has only been settled in the last few years.

The early work in this field has been summarized by Lu and Donohue[51]. Since 1944, the controversy has revolved around the two structures shown in Figure 1.

Figure 1

Figure la. may be regarded as a slightly distorted tetrahedron of sulfur atoms with nitrogen atoms added out from four of the edges, forming a square. Figure lb. is spatially the same, with the roles of the atoms reversed. Also in Figure lb. the nitrogen atoms on the same side of the plane of the sulfur atoms are bound to each other.

The structure in Figure lb, hereafter called the coplanar sulfur structure, was proposed by Hassel and Viervoll[42] on the basis of electron diffraction data. Further evidence for it was put forth by Lippencott and Tobin[49] on the basis of infrared and Raman studies. Their assignment was based on indications of moderately high symmetry and the Raman line at 888 cm.$^{-1}$, which they compared to the line ascribed to the nitrogen-nitrogen bond in hydrazine, which appears at 893 cm.$^{-1}$ Since the spectra of tetrasulfur tetraimide, $S_4N_4H_4$, were similar, the authors concluded that the two compounds had analogous molecular structures, with the nitrogen-nitrogen bond being broken to form nitrogen-hydrogen bonds.

The proposed structure also had the feature of having the nitrogen and the sulfur exhibiting their normal valencies.

The structure in Figure la, hereafter called the coplanar nitrogen structure, was originally proposed by Lu and Donohue[51], also on the basis of electron diffraction studies.

Clark[22] also arrived at this structure from a partial x-ray diffraction study. This structure was confirmed by Sharma and Donohue[66] in 1963 by a three-dimensional refinement of the x-ray data.

The coplanar nitrogen structure of Sharma and Donohue has a few salient features which are worth considering.

As a good approximation, the direct sulfur-nitrogen bond lengths are all equal, with an average value of 1.616 ± .01Å. This may be compared to the sulfur-nitrogen single bond distance (in sulfamic acid $H_3\overset{\oplus}{N}-SO_3^{\ominus}$) of 1.764 ± .02Å. and the single bond radius sum of 1.74Å.[66]

The intramolecular sulfur-sulfur distance of the sulfur atoms on the same side of the nitrogen plane is approximately equal to 2.58Å. The value is considerably shorter than the sum of the Van der Waals radii but somewhat longer than the sulfur-sulfur single-bond distance of 2.05Å.

The respective bond angles are 105° at the sulfur (NSN) and 113° at the nitrogen (SNS).

Attempts to explain these parameters in a consistent theoretical framework have been the object of considerable interest in the last few years.

B. Electronic Structure

Becke-Goehring[8,40] made some of the earliest attempts at a qualitative approach to the electronic structure of S_4N_4, by representing it as a resonant hybrid, of which the most important forms are given in Figure 2.

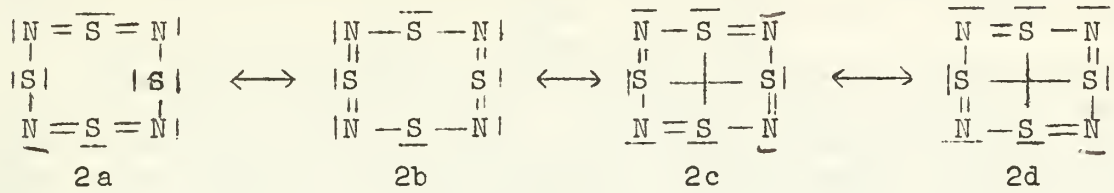

Figure 2

Structures 2a and 2b were the primary contributors.

These assignments were mostly deduced from chemical evidence which centers around hydrolysis reactions and consequently will be discussed with the reactions of S_4N_4.

Sulfur-nitrogen compounds are considered in Craig's formulation of aromatic character in inorganic systems[27,28,29]. He proposes a cyclic delocalization model for S_4N_4 involving p π orbitals on the nitrogen atom and d π orbitals from the sulfur atom. The neighboring nitrogen atom causes promotion from a sulfur atom with sp^3 hybrids to one utilizing a d orbital, thus leaving one or two d orbitals free for delocalization.

If the sulfur atom has strongly electronegative exocyclic groups, the promotion to the state with available d orbitals is favored. The greater the electronegativity difference, the better the contraction of the d orbitals to a size where they may efficiently overlap with nitrogen p π orbitals. A concomitant effect is a tighter binding of the sulfur lone pair and hence less delocalization. Thus $S_4N_4F_4$ has a localized, double-single bond arrangement.

Some experimental justification for the delocalized model can be sited from electron spin resonance studies on S_4N_4 ions[18]. The spectrum consists of nine lines of intensities close to 1:4:10:16:19:16:10:4:1, which is consistent with delocalization involving four equivalent nitrogen atoms. Of course, the possibility of the ion being delocalized while the parent molecule is not must be noted.

A somewhat different approach to the bonding in S_4N_4 has been suggested by Lindqvist[46]. The observed sulfur-sulfur bond lengths in $S_2O_6^{=}$ and $S_2O_4^{=}$ are longer than the generally accepted sulfur-sulfur single bond length. Lindqvist maintains that the true sulfur-sulfur single bond length is longer than the generally assumed 2.05Å., and that the sulfur-sulfur bond length in S_4N_4 is what one would expect for a bond of zero s character, i.e. pure p orbitals between the sulfur atoms. In this case, there wouldn't be any resonance forms and the molecule would have the highly polar structure pictured in Figure 3.

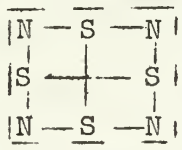

Figure 3

The first attempt towards a more quantitative approach was undertaken by Chapman and Waddington[19]. They consider a delocalized model, with the behavior of the π electrons being approximated by a free electron on a sphere. They solved the Schrödinger equation for a particle on a sphere. Their energy-level and scheme successfully predicted the main absorption band ($\lambda_{calc.}$ = 2560Å., $\lambda_{obs.}$ = 2530Å.). They were also able to accommodate negative ions in their scheme and make predictions as to the magnetic characteristics of the species.

This model has been critized[17,68] on various grounds. It is inconsistent with the observed dipole moment; it can't predict the lower energy absorption spectra bands; and it allows for both sulfur-sulfur and nitrogen-nitrogen bonds. Turner[68] says that in light of similar calculations (e.g. for CH_4), the agreement with the observed spectrum seems fortuitous.

Braterman[17] has applied the formalism of Craig to a study of the visible and ultra-violet spectra of S_4N_4. He considers a model with hybrid orbitals from the nitrogen s and p orbitals and sulfur s, p and d orbitals. The energy-level scheme obtained from simple Hückel molecular orbital calculations has been used to assign the different bands in the spectrum. Braterman found that the spectrum could not be adequately explained without the inclusion of some sulfur-sulfur bonding, and he assigned the major absorption band to a sulfur-sulfur $\sigma \rightarrow \sigma^*$ transition. He also concluded that observation of bands arising from sulfur d orbital interactions makes it unnecessary to accept Lindqvist's highly polar structure.

A more detailed set of calculations has been performed by Turner and Mortimer[68] using extended Hückel molecular orbital calculations employing a limited Slater orbital basis set including 2s and 2p orbitals on the nitrogen and 3s, 3p and 3d orbitals on the sulfur atom.

The first result obtained was the comparison of energies obtained for the coplanar nitrogen and coplanar sulfur (recalling Figures 1a and 1b) models. The coplanar nitrogen structure was shown to be of appreciably lower energy and the nitrogen-nitrogen bond order was shown to be essentially zero under all variation of parameters. Thus both the theoretical and the experimental approaches confirm the coplanar nitrogen structure.

The calculations also indicate a sulfur-sulfur bond order of 0.47 to 0.36. Although d-orbital contributions were found to enhance the bond order, they were not required for a non-zero sulfur-sulfur bond order. The maximum d-orbital charge density was calculated to be 0.160 for dxy orbitals. Thus the d-orbital contribution is principally involved in the sulfur-nitrogen, not the sulfur-sulfur, bond.

The inclusion of sulfur d orbitals was found to lower the energy in the energy level scheme but not to change the order. Thus sulfur d orbitals are contributors but are not major factors in describing the electronic structure of S_4N_4.

IV. Chemical Behavior of the S_4N_4 Ring System

A. Hydrolysis[39,57]

Tetrasulfur tetranitride readily undergoes base hydrolysis.

$$2S_4N_4 + 6OH^- + 9H_2O \longrightarrow 2S_3O_6^{=} + S_2O_3^{=} + 8NH_3$$

This result is typical for a substance with sulfur in the +3 oxidation state, since it can easily undergo disproportionation to sulfur(IV) and sulfur(II).

Other degradative reactions also show the sulfur atom in S_4N_4 to be in the +3 oxidation state.

$$S_4N_4 + 20HI \longrightarrow 4H_2S + 4NH_3 + 10I_2 \quad [55]$$

$$S_4N_4 + 6[O] + 10H_2O \longrightarrow 4H_2SO_4 + 4NH_3 \quad [56]$$

a) Chloramine-T oxidation

Acid hydrolysis is also exhibited[57] by S_4N_4, but at a slower rate.

Another important conclusion which can be drawn from these studies is the fact that all the nitrogen is converted to ammonia, and hydrazine is never observed, whereas the products contain sulfur-sulfur bonds.

B. Reduction[5]

Reduction of S_4N_4 by a variety of reagents results in the formation of tetrasulfur tetraimide.

$$S_4N_4 \xrightarrow{SnCl_2} S_4N_4H_4$$

Tetrasulfur tetranitride may be regenerated by the actions of various oxidizing agents or other sulfur nitrogen compounds.

$$S_4N_4H_4 + 2Cl_2 \longrightarrow S_4N_4 + 4HCl$$

$$3S_4N_4H_4 + 4S_3N_3Cl_3 \longrightarrow 6S_4N_4 + 12HCl.$$

As shown by the crystal structure determination, the conformation of the ring system in $S_4N_4H_4$ is considerably different from that of S_4N_4.[64]

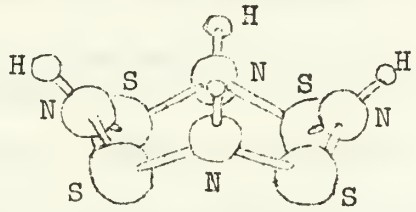

Figure 4

In $S_4N_4H_4$, there exists a regular puckered eight-membered ring of alternating sulfur and nitrogen atoms, with the plane of the nitrogen atoms above the plane of the sulfur atoms. The hydrogen atoms are bound to the nitrogen atoms. The position of the hydrogen atom was deduced from infrared[49] and chemical data[1] and from packing considerations in the crystal.[64]

Tetrasulfur tetraimide is remarkably similar to the S_8 molecule with alternating sulfur atoms replaced by -NH groups. The sulfur bond angles in $S_4N_4H_4$ and S_8 are very close, being 108.4° in the former and 107.8° in the latter. The parallelism is also reflected in the fact that the ultra-violet spectra of these two molecules are very similar[34]. These similarities have led to the designation of $S_4N_4H_4$, along with S_7NH and $S_6(NH)_2$, as "pseudo-sulfurs".

The sulfur-nitrogen distance is 1.674Å., which is larger than the sulfur-nitrogen distance in S_4N_4 (1.616Å.) but shorter than the expected single-bond distance of 1.74Å. This fact, coupled with the lack of basicity of the nitrogen atoms (it is only attacked slowly by strong acids), suggests the possibility of some donation of the nitrogen electron density to energetically favorable sulfur d-orbitals[64].

C. Negative Ion Formation.

When S_4N_4 is treated with vacuum-distilled potassium in dry dimethoxyethane, various color changes are observed[18]. A red diamagnetic solution appears first and is followed by a green coloration which gives rise to the electron spin resonance previously mentioned. Further reaction with potassium causes an increase in spectrum intensity, after which this drops to zero and finally increases again. This behavior has been interpreted as indicating the formation of the following sequence of ions: $S_4N_4^- \rightarrow S_4N_4^{2-} \rightarrow S_4N_4^{3-} \rightarrow S_4N_4^{4-}$.

A solid salt of S_4N_4 was prepared by Becke-Goehring[7] by the reaction of triphenylmethyl sodium and $S_4N_4H_4$ in dioxane-ether solution. Again, a series of color changes was noted (green → yellow → orange → red). The compound is unstable and much more reactive than the imide.

The reaction of $LiAlH_4$ with $S_4N_4H_4$[4] has produced a very explosive compound which analyzed as $LiAlS_4N_4$. The observation that gentle hydrolysis of this compound regenerated $S_4N_4H_4$ led Becke-Geohring to propose the structure in Figure 5.

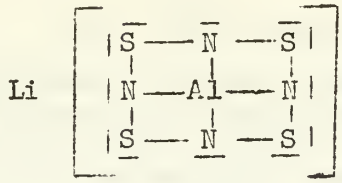

Figure 5

D. Organic Derivatives.

The only organic derivatives of the eight-membered sulfur-nitrogen ring system are the nitrogen substituted derivatives. There are two general routes to these derivatives.

The first approach is the reaction of $S_4N_4H_4$ with various organic reagents which react with secondary amines[1].

$$S_4N_4H_4 + 4\emptyset NCO \longrightarrow (SN\overset{O}{\overset{\|}{C}}NH\emptyset)_4$$

The other approach is to allow sulfur dichloride to react with primary amines.

$$SCl_2 \xrightarrow{\emptyset CH_2NH_2} S_4(NCH_2\emptyset)_4\ ^{11} + S_5(NCH_2\emptyset)_3\ ^{63}$$

$$SCl_2 \xrightarrow{CH_3NH_2} [CH_3NS]_x,\ S_4(NCH_3)_4,\ (CH_3N)_3S_5 \text{ (two isomers)}^{67}$$

E. Degradation to Other Sulfur Nitrides.

Tetrasulfur tetranitride can be transformed into other sulfur nitrides by heating under appropriate conditions[9].

$$S_4N_4 \underset{}{\overset{300°C,\ .01\ mm\ Hg.}{\rightleftharpoons}} S_2N_2 \xrightarrow{27°C} [SN]_x$$

Disulfur dinitride, S_2N_2, is considered to have a linear molecular structure. It is only stable at low temperatures and rapidly polymerizes at room temperature to the dark blue $[SN]_x$.

Polysulfur nitride, $[SN]_x$, is considered to be a long chain polymer. It has been described by simple Hückel molecular orbital theory[20]. It was concluded that bond-length alteration was probably present. The observed spectral and semiconductor properties have been related to this model[21].

Tetrasulfur dinitride, S_4N_2, can be prepared from S_4N_4, by heating or by reaction with CS_2.

$$S_4N_4 \xrightarrow{115°} S_4N_2 + N_2\ ^{54}$$

$$S_4N_4 + 2CS_2 \xrightarrow{100°} S_4N_2 + 2S + 2(SCN)\ ^{34}$$

A cyclic structure has been proposed on the basis of spectral similarities to other cyclic sulfur nitrides. The tetrasulfur diimide can be prepared from S_4N_2 with either $SNCl_2$ or $LiAlH_4$.[34]

F. Halogenation[37]

1. Fluorination

a. Elemental fluorine, even when diluted with nitrogen is too reactive and leads to degradation

$$S_4N_4 \xrightarrow[0°]{F_2} SF_6,\ SF_4,\ NF_3,\ N_2F_4,\ NSF,\ SF_5\text{-}NSF_2\ ^{25}$$

b. The ring may be fluorinated by the action of silver difloride.

$$S_4N_4 \xrightarrow{AgF_2} S_4N_4F_4.$$

Molecules of tetrathiazyl fluoride, $S_4N_4F_4$, have a puckered eight-membered ring of alternating sulfur and nitrogen atoms, with the nitrogen atoms above and below the plane of the sulfur atoms[76]. This one of the few eight-membered sulfur-nitrogen rings with the exocyclic groups bound to the sulfur atoms.

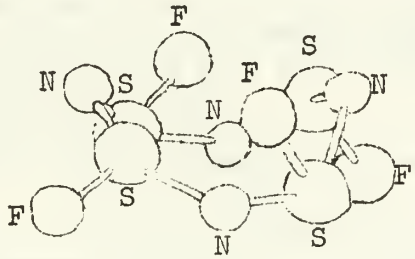

Figure 6

An interesting feature of this structure is that there are alternating sulfur-nitrogen bond lengths, 1.65Å. and 1.55Å.[78] This implies a localized electronic structure for $S_4N_4F_4$.

Reaction of BF_3 [35] and $S_4N_4F_4$ leads to an unstable green adduct, $S_4N_4F_4 \cdot BF_3$. It can be decomposed by heating in a vacuum to form thiazyl fluoride, NSF.

$$S_4N_4F_4 \xrightarrow[\text{vacuum}]{300^\circ} 4NSF$$

2. Chlorination

The action of different chlorinating agents on S_4N_4 leads to different degrees of ring contraction, a common phenomenon in sulfur-nitrogen chemistry.

a. Seven-membered Ring Formation.

Thiotrithiazyl chloride, S_4N_3Cl, which is the most stable cyclic derivative of S_4N_4, may be formed in a variety of reactions; in fact, all the known sulfur-nitrogen chlorides may be transformed into it[37]. It also is formed from the reaction of S_4N_4 with various chlorinating agents.

$$3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$$

$$S_4N_4 \xrightarrow{CH_3\overset{O}{\overset{\|}{C}}-Cl} S_4N_3Cl \text{ [52]}$$

The reaction with S_2Cl_2 is complicated and presumably has several intermediates, as shown by experiments using $^{35}S_2Cl_2$.[8]

Thiotrithiazyl chloride may be converted back to S_4N_4 by heating in a vacuum and reaction with ammonia[13] or aluminum azide.[14]

Thiotrithiazyl chloride is an ionic compound containing the $[S_4N_3]^+$ cation. Several anions may be substituted for the chloride ion. The structure of the $[S_4N_3]^+$ cation is shown in Figure 7.

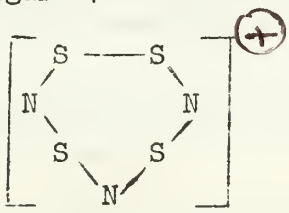

Figure 7

This structure was first proposed by Becke-Goehring on the basis of chemical evidence[12], and it has been confirmed by nitrogen-15 nuclear magnetic resonance[50] and x-ray crystal structure determination[26].

The thiotrithiazyl cation is the only known planar sulfur-nitrogen ring system. The nitrogen-sulfur distances are equal to 1.55Å. and the sulfur-sulfur distance is 2.06Å., which corresponds to a sulfur-sulfur single bond length.

The short sulfur-nitrogen bond length and the planarity of the system have suggested a delocalized structure over all the ring except across the sulfur-sulfur bond. Hückel molecular orbital calculations have been shown to be consistent with this model and give qualitative agreement with the main features of the absorption spectra[43].

b. Six-membered Ring Formation.

Chlorination with elemental chlorine produces trithiazyl chloride.

$$S_4N_4 \xrightarrow{Cl_2} S_3N_3Cl_3$$

The molecular structure of $S_3N_3Cl_3$ is a six-membered ring in the chair form. The chlorine atoms are bound to the sulfur atoms. The chlorine atoms are all cis (Figure 8). The sulfur-nitrogen bond lengths are all equal to 1.605Å.[77] Thus a delocalized electronic structure may be expected.

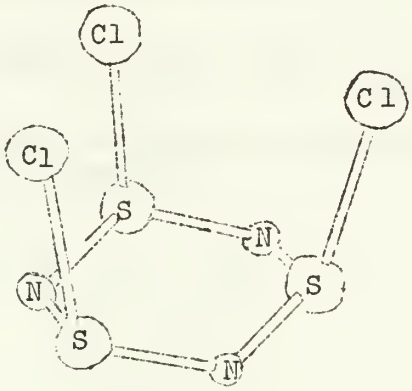

Figure 8

Trithiazyl fluoride cannot be made directly from S_4N_4, but it can be easily prepared from $S_3N_3Cl_3$ by the action of silver difluoride. Fluorine-19 nuclear magnetic resonance[62] studies show that the fluorine atoms also are cis. A full structure determination of $S_3N_3F_3$ would be of interest to see if an isolated single-double bond structure is present here as in $S_4N_4F_4$.

c. Miscellaneous Thiazyl Chlorides[8,37]

If S_4N_4 is allowed to react with S_2Cl_2 in the cold (as opposed to heating which produces S_4N_3Cl), thiodithiazyl chloride, S_3N_2Cl, is formed. It is also formed from the reaction of S_4N_4 with nitrosyl chloride, NOCl.

Thiodithiazyl dichloride, $S_3N_2Cl_2$, is not available directly from S_4N_4, but it is obtained from the reaction of S_2Cl_2 on $S_3N_3Cl_3$.

The nature of these unstable compounds is completely unknown at the present time.

3. Bromination.

The reaction of bromine with S_4N_4 in CS_2 leads to a compound $[SNBr]_x$, the molecular weight of which is unknown.

4. Iodination.

There are no reported iodine derivatives of S_4N_4.

G. Adduct Formation.

Along with halogenation, the most widely studied reactions of S_4N_4 are adduct formations. The general reaction is: S_4N_4, acting as a Lewis base through the nitrogen atoms, adds some Lewis acid in the stiochiometry of 1:1 up to 1:4.

1. SO_3 Adducts.

Two adducts of SO_3 may be isolated, $S_4N_4 \cdot 2SO_3$ and $S_4N_4 \cdot 4SO_3$. The latter compound can react further with SO_3 to yield $S_3N_2O_5$ which is formulated, on the basis of chemical evidence[5], as the sulfur-nitrogen-oxygen ring system depicted in Figure 9.

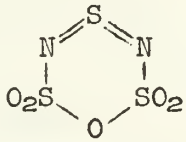

Figure 9

This compound may also be prepared from S_4N_4 by another route.

$$S_4N_4 \xrightarrow{SOCl_2} S_3N_2O_2 \xrightarrow{SO_3} S_3N_2O_5 \quad ^{10}$$

The molecular structure of $S_3N_2O_2$ has been determined by x-ray crystallography[72] and is shown in Figure 10

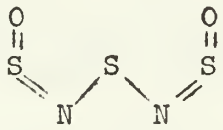

Figure 10

2. BF_3 Adducts.

Tetrasulfur tetranitride forms an unstable, poorly defined adduct with BF_3 of the composition $4S_4N_4 \cdot BF_3$.

3. Thiazyl Fluoride Adducts.

The action of various fluorinating agents on S_4N_4 yields thiazyl fluoride adducts which decompose on heating to thiazyl fluoride.[24]

$$S_4N_4 \xrightarrow{IF_5} I_2 + S_4N_4(NSF)_4 \xrightarrow{50^\circ} NSF$$

4. Metal Halide Adducts.

Adducts formed from S_4N_4 and a metal halide functioning as a Lewis acid have been known for a long time. They are much more stable than other adducts of S_4N_4, and consequently a large number of them have been prepared[58].

One of the easiest adducts to be prepared was $S_4N_4 \cdot SbCl_5$. The structure of this compound (Figure 11) has been determined by x-ray crystallography[59].

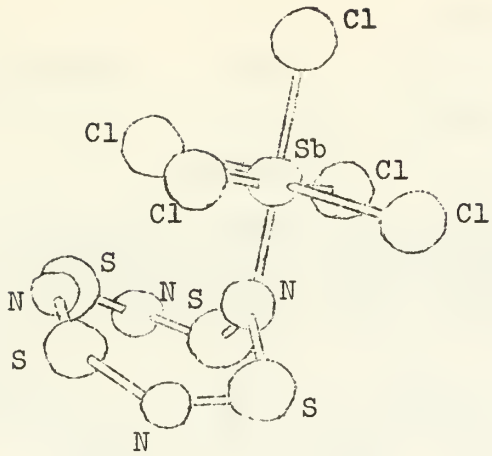

Figure 11

Since S_4N_4 is acting as a Lewis base, electron density is drained from the ring causing the sulfur-sulfur bonds to weaken. Thus a conformational change is possible. The ring now adopts the same conformation as $S_4N_4F_4$. The $SbCl_5$ is coordinated to one of the nitrogen atoms. The sulfur-nitrogen bond lengths from the nitrogen atom coordinated to the antimony are considerably lengthened to 1.74Å.

The knowledge of this structure led to some interesting predictions as to the structures of other metal halide adducts of S_4N_4[59], for example: two S_4N_4 rings <u>trans</u> to each other in an octahedron about a metal atom, e.g., $2S_4N_4 \cdot SNCl_4$ and S_4N_4 acting as a bidentate ligand, through two opposite nitrogen atoms, e.g., $WCl_4 \cdot S_4N_4$, $VCl_4 \cdot S_4N_4$.

Another route to metal halide adducts to metal halide adducts is through the reaction of metal halides with $S_3N_2O_2$.[15]

$$S_3N_3O_3 \xrightarrow{SbCl_5} S_4N_4 \cdot SbCl_5$$

$$S_3N_2O_2 \xrightarrow{TiCl_4} S_4N_4 \cdot 2TiCl_4$$

An interesting structure has been proposed for this last compound[15]. It consists of a dimer of titanium atoms each in an octahedral environment with two bridging chlorines and a bridging S_4N_4.

Obviously, further structural studies, especially of the "bidentate" species, would be desirable.

H. Reaction with Thiophilic Reagents.

If S_4N_4 were to act as a Lewis acid, then the attack would be on the sulfur atom. Apparently, there aren't any simple adducts stable enough to be isolated. Rather the ring goes through ring construction or degradation to a linear molecule. This behavior has already been noted in halogenation reactions.

Triphenyl phosphine and triphenyl phosphine methylene react with S_4N_4[45,31] by attacking the sulfur atom.

$$S_4N_4 + 2P\phi_3 \longrightarrow SP\phi_3 + \phi_3PN_4S_3$$

The following structures have been proposed for $\phi_3PN_4S_3$.[31]

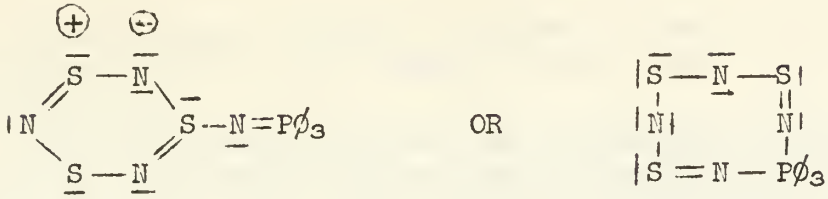

Figure 12

The reaction of S_4N_4 with KCN[31] is more complex. By analogy with its reaction with S_8, the cyanide ion is assumed to attack the sulfur atom. The compound isolated is $K_2(C_2N_{10}S_6)\cdot 2KCN$, which has been formulated as containing the following anion.

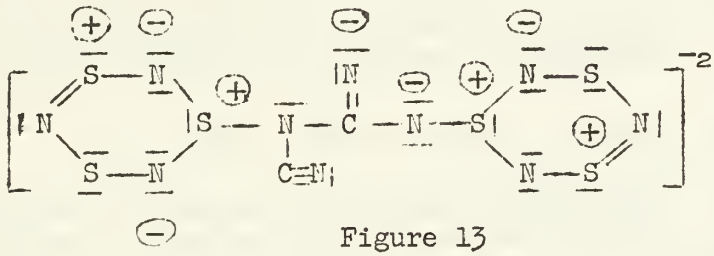

Figure 13

Reaction with Grignard reagents cause ring degradation[74].

$$\phi MgBr \xrightarrow{S_4N_4} \phi SN{=}S{=}NS\phi$$

Complete degradations have been observed in the reactions of S_4N_4 with PCl_3[36] and ϕPCl_2.[32]

4. NH_3 Adducts[5].

One mole of ammonia adds to S_4N_4 to give a compound of the composition $S_4N_4\cdot NH_3$, but this compound is identical to the adduct of S_2N_2 with ammonia. It is assumed, therefore, that the ring was cleaved during the reaction.

I. Formation of Metal Thionitrosyl Complexes[5].

The large number of metal thionitrosyl complexes which have been prepared would take up more space than is available in this seminar. More complete compilations may be found elsewhere[6]. I shall only outline preparative procedures and discuss a few compounds which have been more intensively investigated.

The first method of preparation involves the reaction of metal ions with S_4N_4 in liquid ammonia. In view of the work done on NH_3 adducts of S_4N_4 it is probable that $N_2S_2\cdot NH_3$ is the source of the ligand. A typical example is the formation of the lead complex.

$$PbI_2 \xrightarrow[NH_3(l)]{S_4N_4} Pb(NS)_2$$

The molecular structure of this compound has been determined by x-ray crystallography and is pictured in Figure 14.

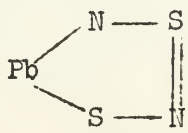

Figure 14

The sulfur-nitrogen distances are reported from 1.60 – 1.70A., but due to the limited nature of the investigation nothing except the stereochemistry should be relied upon.

Many thionitrosyl complexes can also be prepared from $S_4N_4H_4$. Both simple and more complex species, such as $Hg_5(NS)_8$, can be prepared.

Group 8 transition metals readily form thionitrosyl complexes from S_4N_4. These compounds were originally assumed to have the composition $M(SN)_4$, but later work[61] has shown that a variety of ligands are formed, the most common of which gives the molecular formula, $M(HN_2S_2)_2$.

There are two general routes to these complexes from S_4N_4: first, the reaction of an anhydrous metal halide with S_4N_4 in refluxing alcohol; secondly, the reaction of S_4N_4 with metal carbonyls in an inert solvent.

A more intensive study of the reaction of S_4N_4 with $NiCl_2$ in alcoholic solution showed a series of compounds to be formed.

$$NiCl_2 + S_4N_4 \xrightarrow{ETOH} NiS_4N_4H_2,\ NiS_5N_2H,\ NiS_6N_2.$$

These compounds were separated chromatographically. The hydrogen was obtained from the solvent, since no product was obtained with reaction in CS_2 or benzene

The hydrogen was shown to be attached to the nitrogen from the infrared spectra of $NiS_4N_4H_2$ and $NiS_4N_4D_2$.

The protons in $NiS_4N_4H_2$ are fairly acidic and consequently derivatives have been made by various routes.

$$Ni(HN_2S_2)_2 \xrightarrow{AgNO_3} \xrightarrow{CH_3I} Ni(CH_3N_2S_2)_2$$

a) monomethyl and dimethyl compound.[73]

$$Ni(HN_2S_2)_2 + \emptyset Li \longrightarrow Ni(\emptyset N_2S_2)_2 + LiH \ ^{75}$$

The molecular structure of the dimethyl compound has been determined by x-ray crystallography[73], and has been found to be square planar in the <u>trans</u> configuration, with methyl groups bound to the nitrogen atoms coordinated to the nickel atom.

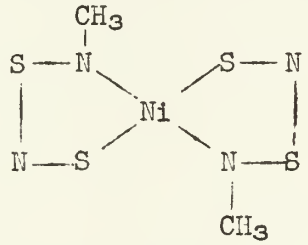

Figure 15

The structure of $Ni(HN_2S_2)_2$ has not been determined but that of the platinum compound, $Pt(HN_2S_2)$ has been determined[47,48]. In contrast to the dimethyl nickel compound, the configuration is <u>cis</u> coplanar. The assignment of the hydrogen atom as being on the nitrogen atom coordinated to the metal atom was done from a space model[48] of the structure and consequently is a tentative assignment.

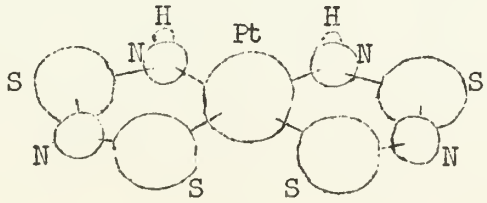

Figure 16

J. Sulfur in Higher Oxidation States.

The only eight-membered sulfur-nitrogen ring with sulfur in an oxidation state greater than +3 which is directly available from S_4N_4 is $S_4N_4F_4$.

A tetrameric thionylimide can be produced by the air oxidation of $S_4N_4H_4$.

$$S_4N_4H_4 \xrightarrow[110\text{-}20^\circ]{O_2} (OSNH)_4 \quad ^{30}$$

This compound readily polymerizes. The polymer can regenerate S_4N_4 by hydrolysis.[65]

$$6[OSNH] + H_2O \longrightarrow S_4N_4 + 2NH_4HSO_4.$$

The formation of a derivative of a tetramer sulfimide (sulfur in the +6 oxidation state) from an existing ring system has not been reported, but the compound has been formed from SO_3 and ammonia.[70]

$$SO_3 \xrightarrow{NH_3} (NH_4)_2S_3O_{10} \xrightarrow[H_2O]{AgNO_3} [AgNSO_2]_4$$

V. Conclusion

As we have seen, S_4N_4 has proved to be an interesting and versatile compound, both in a study of its physical characteristics and as an entry into several other interesting chemical systems.

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SOME RECENT ADVANCES IN THE CHEMISTRY OF THE ANHYDROUS METAL NITRATES

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Introduction

The preparation of an anhydrous metal nitrate was first reported as early as 1909[1]. More recently the nitrates of the Lanthanide group were prepared by Moeller[2], but it was in 1957, with the report of the preparation of volatile anhydrous copper (II) nitrate, by Addison[3], that a serious investigation into the properties of the anhydrous nitrates was begun. Until the discovery of the volatile nature of anhydrous $Cu(NO_3)_2$, implying strong covalency in the metal-ligand bond, the interaction of the nitrate group with a metal was generally believed to be of an ionic nature. This conclusion was reached, however, only from a consideration of nitrates in the presence of water. In aqueous solution, nitrates generally exist as the ions, and the NO_3^- ion acts as a very weak coordinating agent.

Attempts to dehydrate hydrated salts, such as $Cu(NO_3)_2 \cdot 6H_2O$, result in decomposition before the pure anhydrous nitrate is obtained. Only with metals of Group IA and IIA, where we would expect the most ionic nitrates, can anhydrous nitrates be prepared with ease and without decomposition.

It is the purpose of this seminar to examine some recent developments that indicate the nature of the NO_3 group in the anhydrous metal nitrates.

Preparation

There are four primary reagents used to prepare anhydrous metal nitrates. The successful use of each one varies widely, depending upon the specific technique.

(A) Nitric Acid

The oldest but least effective method, in so far as the synthesis of anhydrous nitrates is concerned, involves the use of aqueous nitric acid. With this reagent, the hydrated nitrates can be obtained for the great majority of the metals, but great difficulty is encountered in obtaining complete dehydration, even under severe conditions. The anhydrous nitrates of many of the Group I and II metals can be obtained by dehydrating their hydrated nitrate salts, but in general this technique leads to decomposition to the nitrite or oxide before the pure anhydrous nitrate is obtained. Therefore this technique is seldom used.

(B) Dinitrogen (V) Pentoxide

Dinitrogen (V) pentoxide, together with nitric acid, was first used by Guntz and Martin[1] in 1909 to produce anhydrous nitrates by dehydration of the hydrated nitrates of dipositive manganese, copper, nickel and cobalt. More recently, liquid dinitrogen (V) pentoxide has been allowed to react with a variety of metal oxides and chlorides to prepare the anhydrous nitrate. This work was done by Schmeisser and his co-workers[4]. Field and Hardy[5,6] have used a similar method to prepare the anhydrous nitrates of many more transition metals. Recently, Addison[7] used a dilute solution of the oxide in carbon tetrachloride to prepare the anhydrous chromium (III) nitrate from chromium

hexacarbonyl, and slightly later the volatile anhydrous tin (IV) nitrate from tin (IV) chloride with the oxide[8]. Chromium (III) nitrate is obtained as such and not as a dinitrogen (V) pentoxide adduct. Yet in an identical reaction using dinitrogen (IV) tetroxide, the 1:2 adduct, $Cr(NO_3)_3 \cdot 2N_2O_4$, is obtained. From this adduct, only one mole of dinitrogen (IV) tetroxide can be removed.

Bagnall and co-workers[9] were able to prepare cesium hexanitrato tin (IV) using dinitrogen (V) pentoxide,

$$Cs_2SnCl_6 \xrightarrow{N_2O_5} Cs_2Sn(NO_3)_6$$

but the hexanitrato complexes of the other Group IVA elements were not obtained.

(C) Dinitrogen (IV) Tetroxide

The most widely used and most effective reagent for the preparation of the anhydrous nitrates is nitrogen (IV) oxide. The exact method of preparation varies, depending upon the reactivity of the metal or metal compound used. One of the earlier methods involved simply mixing the metal oxide with liquid dinitrogen (IV) tetroxide and heating in a closed system. Gibson[10,11] prepared the anhydrous nitrates of several metals in the first transition series, including that of copper, but was unaware of any property of volatility. Using a similar method, Moeller[2] and workers prepared the anhydrous nitrates of the lanthanide elements. Since then the approach of using an NO_2-N_2O_4 mixture alone has given way to the use of dinitrogen (IV) tetroxide dissolved in an electron donating solvent, such as ethyl acetate. Addison has prepared a wide variety of anhydrous nitrates in this way. A typical example is the formation of the nitrates of the Group II metals[12].

$$MCl_2 \xrightarrow[\text{in } N_2O_4]{\text{20\% Ethyl Acetate}} M(NO_3)_2 \cdot XN_2O_4 + NOCl$$

Many of these reactions occur at room temperature. Less reactive chlorides can sometimes be converted by heating or by using a more polar solvent, such as dimethyl sulfoxide.

One unusual adaption to this general technique is the use of the metal carbonyl as a starting material. Here the reaction is generally carried out in a diluting solvent such as carbon tetrachloride, since the reaction can be explosive. The compound $Fe(NO_3)_3 \cdot N_2O_4$ is one of several adducts that can be prepared both by this procedure and by the dinitrogen tetroxide-ethyl acetate method[13].

$$Fe(CO)_5 \xrightarrow{N_2O_4 \text{ in } CCl_4} Fe(NO_3)_3 \cdot N_2O_4$$

$$\begin{matrix} FeCl_2 \\ FeCl_3 \end{matrix} \xrightarrow{\text{20\% Ethyl Acetate in } N_2O_4} Fe(NO_3)_3 \cdot 1.1N_2O_4 + NOCl$$

The corresponding pure nitrate cannot be obtained by heating the adduct compounds without decomposition.

Bagnall and co-workers[9] succeeded in preparing the hexanitrato complexes $(NMe_4)_2Zr(NO_3)_6$ and $(NMe_4)_2Hf(NO_3)_6$, using the corresponding chloride together with a nitrogen (IV) oxide-acetonitrile mixture. Only tetranitrato zirconium (IV) is obtained with dinitrogen (V) pentoxide.

(D) Chlorine (I) Nitrate

The halogen nitrates are extremely reactive and have been used to prepare anhydrous nitrates, but only to a small extent. At very low temperatures

(~-50°C.), Schmeisser[14] has used chlorine nitrate to prepare the tetranitrato complexes of tin(IV) and titanium(IV). However, because of the danger of explosion, the simpler paths are generally followed.

A complete list of the reported anhydrous nitrates is too long to be included here. However, a more detailed accounting of the preparations of the individual anhydrous nitrates can be found in two review articles[15,16].

Bonding

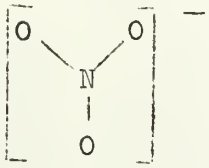
Since the discovery by Addison[3] that copper (II) nitrate is volatile, the nature of the bonding involved in the anhydrous nitrate system has been under continuing investigation. Volatility of a compound is an indication of strong covalency, and attempts have been made to demonstrate both the extent of covalency in the anhydrous nitrates and its effect on the reactivity of these compounds. Several other volatile nitrates have been prepared, as indicated in Table 1.

Compound	Ref.	Compound	Ref.	Compound	Ref.
$Au(NO_3)$	(6)	$Hf(NO_3)_4 \cdot N_2O_5$	(6)	$Ti(NO_3)_4$	(4)
$Fe(NO_3)_3$	(13)	$Pd(NO_3)_2$	(6)	$Zr(NO_3)_4$	(5)
$Fe(NO_3)_3 \cdot N_2O_4$	(13)	$Zn(NO_3)_2$	(6)	$Be_4O(NO_3)_6$	(18)
$Hg(NO_3)_2$	(13)	$Sn(NO_3)_4$	(17)	$In(NO_3)_3$	(6)

Table 1 - Volatile Anhydrous Metal Nitrates

Infrared spectroscopy has been the tool most used to demonstrate the bonding in the anhydrous nitrates. Although it is not able to give a clear and unequivocal picture of the bonding in the system, it has enabled chemists to distinguish between ionic and covalent bonds and to clarify some of the gross features of what has been a confused picture.

The interpreation of infrared data is based upon using a model similar to that of the carbonate ion. In highly ionic crystals, such as the alkali metal nitrates, the symmetry of the NO_3 species is D_{3h}, which indicates that the ion is planar and symmetrically oriented with regard to the three oxygen atoms. Such a configuration



leads to the prediction of six normal modes of vibration, two of which are nondegenerate and two pairs of which are doubly degenerate. The vibration type and activity in the Raman and Infrared spectrum, together with absorption frequencies and assignments are listed in Table 2.[19]

Type	NO_3^-	Raman	IR	$cm.^{-1}$	Assignment
A_1'	ν_1	a	ia	1050	N-O stretch (sym.)
A_2''	ν_2	ia	a	831	NO_2 deformation
E'	ν_3	a	a	1390	NO_2 asym. stretch
E'	ν_4	a	a	720	planar rocking

Table 2 - Vibrations for the Ionic (D_{3h}) Nitrate Ion

Upon formation of a metal-oxygen bond, the symmetry is lowered from D_{3h} to C_{2v}, and the two doubly degenerate bands are split, giving six infrared active, non-degenerate vibrations. Table 3 lists the vibration type and activity in the Raman and Infrared, together with absorption frequencies and assignments for C_{2v} symmetry[20].

Type	ONO_2	Raman	IR	cm.$^{-1}$	Assignment
A_1	ν_3	a	a	~740 (21)	NO_2 bending
A_1	ν_1	a	a	1290-1253	NO_2 sym. stretch
A_1	ν_2	a	a	1034 - 970	N-O stretch
B_2	ν_6	a	a	800 - 781	non-planar rock
B_1	ν_4	a	a	1531-1481	asym. stretch
B_1	ν_5	a	a	~713 (21)	planar rock

Table 3 - Vibrations for the Covalent (C_{2v}) Nitrate Group

The result of forming the metal-oxygen bond is to shift the $\nu_1(D_{3h})$ and $\nu_2(D_{3h})$ bands to lower frequencies and to split the doubly degenerate $\nu_3(D_{3h})$ band into two singly degenerate, widely-spaced bands. The splitting of the degenerate $\nu_4(D_{3h})$ band is, by comparison, quite small. Ferraro[22] has proposed that the size of the splitting of the $\nu_3(D_{3h})$ band into ν_1 and $\nu_4(C_{2v})$ is a measure of the strength of the metal-oxygen interaction, since it has been observed that in going from the ionic alkali metal nitrates (D_{3h}) to covalent methyl nitrate (C_{2v}), the splitting of $\nu_3(D_{3h})$ into ν_1 and $\nu_4(C_{2v})$ goes from 0 to 385 inverse centimeters, respectively. Some typical spectra which demonstrate the gradual shift from D_{3h} to C_{2v} symmetry are described in Table 4.

Compound	Symmetry	ν_1	ν_2	ν_3	ν_4	Ref.
$NaNO_3$	NO_3^--D_{3h}	—	836m	1358vs	N.R.	(21)
KNO_3	"	—	824m	1348vs	733m	(21)
$Cu(NO_3)_2 \cdot 3H_2O$	"	—	836m	1378vs	N.R.	(21)
$Fe(NO_3)_3 \cdot 9H_2O$	"	—	835w	1361vs	N.R.	(20)

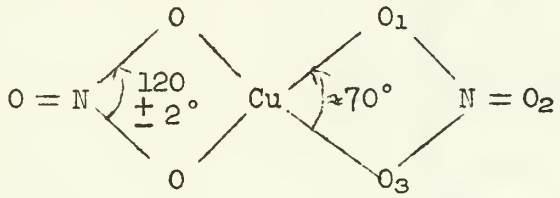
		ν_1	ν_2	ν_3 or ν_5	ν_4	ν_6	Ref.
$Hg(NO_3)_2$	$-ONO_2$ - C_{2v}	1376s	1027vs	750m	1495m	788vs	(20)
$Zn(NO_3)_2$	"	1359s 1300vs	1050sh 1040s	763s 746m	1546s 1502m	800s 793s	(20)
$Mn(NO_3)_2$	"	1294vs	1019vs	759m	1553vs	805s 799vs	(20)
$Cr(NO_3)_3$	"	1283vs 1249vs	1044s 990s	727m	1631s 1560vs 1544vs	782s	(7)
CH_3NO_3	"	1287s	854s	N.R.	1672vs	759m	(19)

(N.R. = Not Reported; m = medium; s = strong; w = weak; sh = sharp; v = very)

Table 4 - Typical Infrared Spectra of Ionic and Covalent Nitrates

The difference between the spectra of the ionic (D_{3h}) and covalent (C_{2v}) nitrates are immediately apparent, and the spectra of the strongly covalent methyl nitrate and of the covalent nitrates are in good agreement.

Since the investigation of the anhydrous nitrates was based upon a study of the copper (II) compound, it was back to this system that workers went to obtain a more detailed understanding of the bonding. Addison[23], in a detailed investigation of the vapor, found gaseous copper nitrate to be both stable above 226 degrees C. and monomeric (by both vapor pressure studies and mass spectrometry)[24]. La Villa and Bauer[25] later determined the molecular structure of the vapor by electron diffraction. They concluded that the copper atom is surrounded by the bidentate nitrate group in a planar arrangement, as shown in Figure 1. [A previous report was in error[26]]



Bond Lengths

$Cu-O_1 = 2.00 \pm 0.02$ Å
$N-O_1 = 1.32 \pm 0.04$ Å
$N-O_2 = 1.28 \pm 0.04$ Å
$Cu-N = 2.30 \pm 0.03$ Å

Figure 1 - Structure of Gaseous Copper (II) Nitrate.

The N-O distances are not the same, but the average 1.30 Å separation is more typical of a covalent nitrate group, as in methyl nitrate where the N-O distance is 1.28 Å., than of an ionic nitrate such as sodium nitrate with an N-O distance of 1.218 Å.[25]

A preliminary crystal structure determination by X-ray diffraction[27] was in error, but a more accurate study by Wallwork[28] led to a structure which can be interpreted as involving pseudo-octahedral (4+1+1) coordination by the copper atom. The structure pictured in Figure 2 consists of chains of copper atoms, bridged by nitrate groups. These chains are roughly parallel, and the copper atoms form a plane perpendicular to the chains. Each copper atom is surrounded by a square-planar array of oxygen atoms from bridging nitrate groups. The third oxygen atom of each bridging nitrate group is located unsymmetrically between the copper atoms. This configuration results in four tightly held oxygen atoms about each copper atom, with two more oxygen atoms at unequal distances, forming a severely distorted octahedron. The length of the strong covalent bonds of the oxygen atoms in the plane vary from 1.92 to 2.02 ± 0.02 Å., whereas the more weakly held oxygen atoms lie at a distance of 2.43 Å. and 2.68 Å. Figure 3 lists the important bond lengths and angles of the nitrate groups surrounding the copper atom.

This crystal structure gave a clear indication of the strong bonding in copper (II) nitrate, but attempts to correlate the infrared spectrum with other physical measurements still gave a confused picture. The reason is the presence of both an $\underline{\alpha}$ and $\underline{\beta}$ form of copper nitrate. The sublimation temperature is a critical factor in determining whether pure $\underline{\alpha}$ or $\underline{\beta}$ or a mixture of the two forms is obtained[29]. The X-ray study mentioned above was done on $\underline{\alpha}$-copper nitrate, whereas the infrared study was done on $\underline{\beta}$-copper nitrate[21]. This report of the two forms of copper nitrate encouraged several authors to make a more detailed examination of the infrared spectrum.

A consideration of the ways in which the nitrate group can bond leads to the models given in Figure 4.

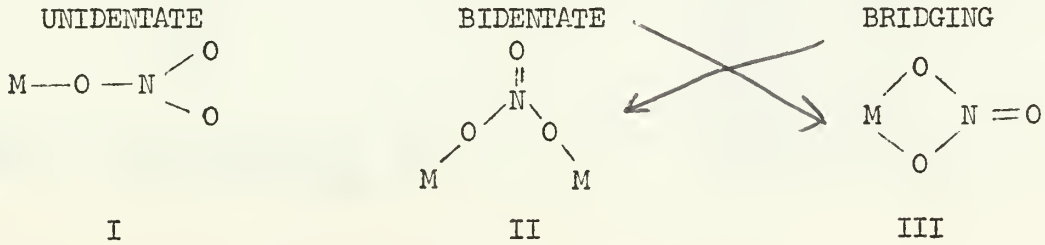


Figure 4 - Three Models of a Nitrate Group Bonding to a Metal.

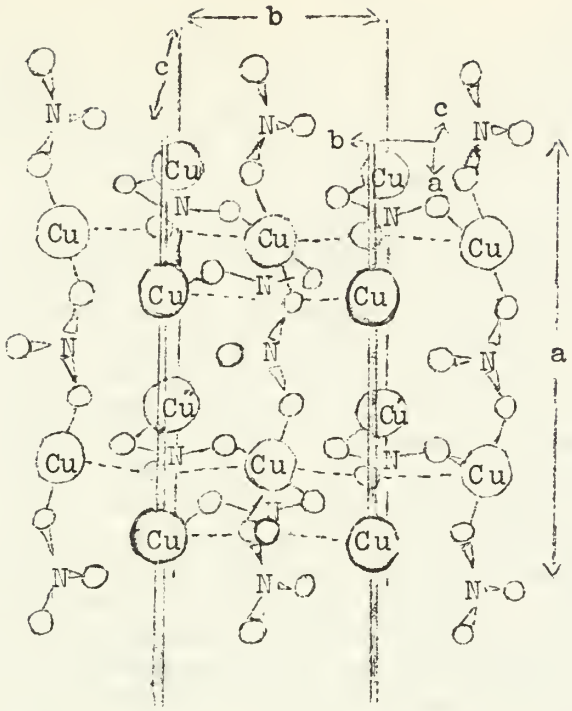


Figure 2 - General view of the structure α-copper (II) nitrate. Broken lines indicate the weaker Cu···O interactions.

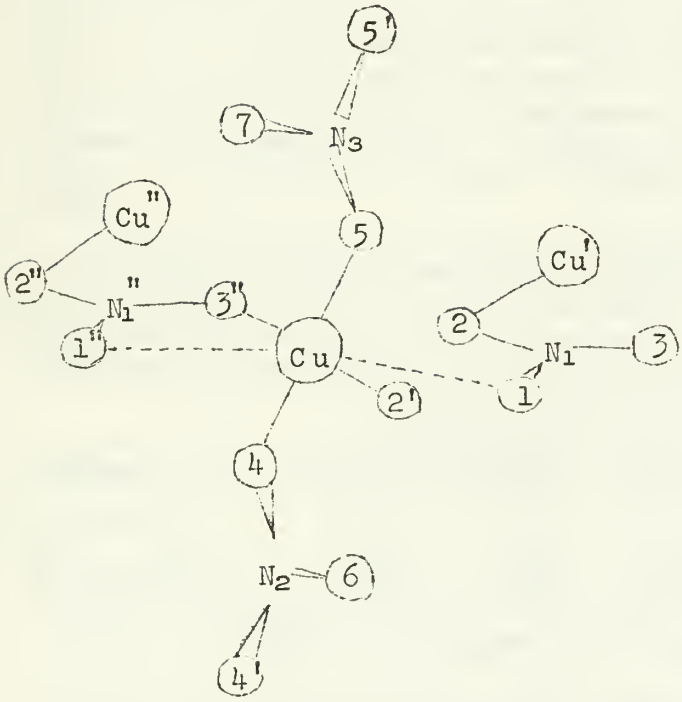


Figure 3 - Bond lengths in (Å) and bond angles.

Bond Lengths in Å ± 0.02Å

$Cu - O_2' = 2.02$
$Cu - O_3'' = 2.02$
$Cu - O_5 = 1.96$
$Cu - O_4 = 1.92$
$Cu - O_1'' = 2.68$
$Cu - O_1 = 2.43$
$N_3 - O_5 = 1.35$
$N_1 - O_1 = 1.16$
$N_2 - O_4 = 1.27$

Bond Angles

$O_5CuO_2' = 92°$
$O_2'CuO_4 = 87°$
$O_4CuO_3'' = 95°$
$O_3''CuO_5 = 88°$
$CuO_1''N_1'' = 78°$
$CuO_4N_2 = 123°$
$CuO_1N_1 = 113°$
$CuO_5N_3 = 113°$
$CuO_3''N_1'' = 110°$

For both models II and III, one would expect a higher-frequency band to appear in the infrared spectrum due to the N=O stretch than would appear in the infrared spectrum of model I. Since the α-copper nitrate structure is known to be bridging, it was expected that the infrared spectrum would contain such a high-frequency band. But the spectrum of α-copper nitrate does not contain any bands above the usual range of 1481-1531 cm.$^{-1}$, which is considered to be the region of the antisymmetric stretch of a unidentate nitrate group[30]. It is possible that the weaker interaction of the third oxygen atom of the bridging nitrate group in α-copper nitrate is strong enough to lower the frequency of the infrared band due to the N=O stretch.

It was noticed early in the investigation of the anhydrous metal nitrates that in certain cases the infrared spectrum contained a strong band above 1600 cm.$^{-1}$, i.e., where the N=O stretching frequency would be expected to occur. It was then proposed that this band was due to the presence of either a bidentate or bridging nitrate group. It has since been found that although the presence of a band at 1600 cm.$^{-1}$ indicates bidentate or bridging nitrate groups, its absence does not preclude the possibility of such groups existing[30]. Cotton has found in an X-ray study of $[(Me_3PO)_2 \cdot Co(NO_3)_2]$ that the nitrate groups are bidentate[31], and the infrared spectrum indicates C_{2v} symmetry with no band above 1520cm.$^{-1}$ [32]. However Addison[21] reported cobalt (II) nitrate to have ionic D_{3h} symmetry, and Cotton[32] suggests that it is possible for the lowering of the symmetry to C_{2v} of $[(Me_3PO)_2 \cdot Co(NO_3)_2]$ to be due to primarily electrostatic forces. If the bonding in this compound is primarily ionic, then one would not expect to observe a strong N=O stretching frequency.

The only simple, confirmed example of bidentate coordination in the solid is that of titanium (IV) nitrate. Addison and Wallwork[33] have reported a preliminary structure determination of this molecule, which indicates that the four nitrate groups are bidentate, with all Ti-O bond lengths the same. The infrared spectrum of titanium (IV) nitrate does have a strong band at 1628 cm.$^{-1}$, which is assigned to the stretching frequency of the terminal N=O groups of the bidentate nitrate[34]. Similar bands in the infrared appear for the tin and zirconium tetranitrates. Field and Hardy[6] suggest that the presence of strong bands at a frequency greater than 1560 cm.$^{-1}$, together with a strong band at 1270 cm.$^{-1}$ indicates a bridging or bidentate nitrate group.

Topping[35] made an attempt to correlate this same idea using a normal coordinate analysis of data for the compound $Rb[UO_2(NO_3)_3]$, in which the nitrate group is known to be bidentate[36], with that of $Cs_2[U(NO_3)_6]$, in which the nitrate group is assumed to be unidentate. The infrared frequencies, together with assignments, are tabulated in Table 5.

	Frequencies and Assignments in cm.$^{-1}$					
Compound	$\nu_4(B_2)$	$\nu_1(B_1)$	$\nu_2(A_1)$	$\nu_6(B_1)$	ν_3 or ν_5	Bonding
$Cs_2[U(NO_3)_6]$	1531	1274	1030	805	734/702	UNIDENTATE
$Rb[UO_2(NO_3)_3]$	1536	1276	1023	803	736/711	BIDENTATE

Table 5 - Spectra and Assignments for $Cs_2[U(NO_3)_6]$ and $Rb[UO_2(NO_3)_3]$.

The spectra of both the ^{14}N and ^{15}N substituted compounds of the rubidium salt are known, and Topping found he could account for the shifts in the infrared spectrum upon substitution of ^{15}N by using a model based on either unidentate

or bidentate coordination. From this, he concluded that the absence of bands above 1560 cm.$^{-1}$ could not be taken as evidence of unidentate bonding. He also suggested that an examination of the far infrared would help clarify the situation, since it is in this region that the metal-oxygen bond stretching frequency is expected to occur. In the unidentate case, there will be only one metal-oxygen stretch, whereas in the bidentate and bridging cases there will be both one metal-oxygen stretch and a rocking mode.

Table 6 contains the frequencies and assignments of the bands below 700 cm.$^{-1}$

	Frequencies and Assignments in cm.$^{-1}$			
Compound	M - O Stretch	Rocking Mode	$(UO_2)^{2+}$	Bonding
$Cs_2[U(NO_3)_6]$	224			UNIDENTATE
$Rb[UO_2(NO_3)_3]$	262	223	212	BIDENTATE

Table 6 - Far Infrared Frequencies and Assignments.

As can be seen from Table 6, the unidentate compound has only a single metal-oxygen stretch, whereas the bidentate compound has both the metal-oxygen stretch and the lower energy rocking mode.

Ferraro[37] has taken the same approach, but his results are far more ambiguous. For the transition metal nitrates, very complicated spectra are observed, making it impossible to use the simple argument of Topping[35]. Table 7 lists a sampling of frequencies from Ferraro's report.

Compound	Sym.	Frequencies from 350 cm.$^{-1}$ - 70 cm.$^{-1}$ (a)
$Cu(NO_3)_2$	C_{2v}	336(s), 299(sh), 253(w,sh), 209(m), 170(w), 138(vw), 94(vw)
$Zn(NO_3)_2$	C_{2v}	317(s,sp), 284(s,sp), 188(w), 141(m,sh), 127(m,sp), 119(m,sh), 96(w,sh)
$Mn(NO_3)_2$	C_{2v}	231(s), 199(sh), 138 (m,sp), 96(w,sh)
$Nd(NO_3)_3$	C_{2v}	226(s), 178(s), 112(sh)
$Li(NO_3)$	D_{3h}	321(s), 275(sh), 166(m,sp), 152(w,sh), 96(w)
$Pb(NO_3)_2$	D_{3h}	226(w,sh), 180(w,sh), 92(s)
$AgNO_3$	D_{3h}	170(s), 125(sh), 103(w), 80(w)
$Ba(NO_3)_2$	D_{3h}	153(m), 94(w), 77(w)

s = strong, sp = sharp, v = very, w = weak, m = medium, sh = shoulder

(a) all strong bands are broad.

Table 7 - Far Infrared Spectra of Covalent and Ionic Nitrates.

All the spectra of the covalent (C_{2v}) nitrates have a strong band in the far infrared above 200 cm.$^{-1}$, whereas this band is absent in the spectra of the ionic (D_{3h}) nitrates, except for lithium nitrate. Lithium has a mass comparable to oxygen, and the resulting coupling of lattice vibration modes makes the interpretation of the far infrared spectrum very difficult. From these data, Ferraro proposes that the presence of a strong band above 200 cm.$^{-1}$ in the far infrared is due to a covalent metal-oxygen bond, but he makes no attempt to distinguish between unidentate and bidentate bonding on the basis of these complicated spectra.

Complications

The investigation of anhydrous metal nitrate systems, using infrared techniques, has been extensive but not rigorous. There are several reasons for this.

The α-copper (II) nitrate system is the only nitrate for which the structure has been completely determined. The infrared spectra of both α- and β - copper nitrate have been reported[30], but the presence of a variety of different modes of coordination by nitrate groups gives rise to extremely complicated spectra. This is true of a large number of the anhydrous nitrates, making interpretation of the spectra, where splitting of the normal bands has occurred, a perilous undertaking. In many instances, electrostatic effects can be important, as mentioned earlier for the spectrum of $[(Me_3PO)_2 \cdot Co(NO_3)_2]$. Buijs and Schutte[38] have suggested the lowering of D_{3h} to C_{2v} symmetry can be due to interactions of the ions within the lattice, rather than to covalency in the metal-oxygen bond. The lowering of the symmetry is not conclusive proof that there is covalent bonding present.

An interesting example is the case of the lanthanide nitrates. Ferraro[39] has reported the infrared spectrum of all of these compound, except cerium and praseodymium nitrate, from 4000 to 100 cm.$^{-1}$. Each of the nitrates has C_{2v} symmetry. The separations of the ($\nu_4 - \nu_1$) bands of the nitrates of praseodymium through erbium are all less than 200 cm.$^{-1}$, a good indication that the metal-oxygen bond is only weakly covalent, which is what one would expect for the predominately ionic lanthanide compounds. However the spectra of terbium, ytterbium, and lutetium nitrates have bands above 1575 cm.$^{-1}$ and large ($\nu_4 - \nu_1$) separations, which we associate with strongly covalent, bridging or bidentate nitrate groups. This is in direct conflict with all we know about bonding in compounds of the lanthanides. Ferraro draws no conclusion from these data, but there is a distinct possibility that the coordination number of the lanthanide ions is greater than six. The effect that additional nitrate groups around the central ion would have upon the infrared spectrum cannot be easily estimated, and conclusions drawn from such evidence alone would be open to question. The increase in effective nuclear charge is another factor operating here and elsewhere, which tends to increase the distortions due to electrostatic effects and lowers the symmetry of the nitrate ion without giving us reason to invoke covalent bonding.

It is not until additional structural evidence becomes available that a definitive interpretation of the infrared data will be possible.

Dinitrogen (IV) Tetroxide Adducts

The anhydrous metal nitrates are usually isolated by heating the adducted species prepared from the reaction of the metal or metal compound with dinitrogen tetroxide. In some instances, the anhydrous, adduct-free compound is obtained, but with others the dinitrogen tetroxide molecules cannot be removed. Where it is possible to remove dinitrogen tetroxide, it is not always possible to recover the original adduct by treatment with dinitrogen tetroxide. Illustrating this difference are the copper nitrate system and the magnesium nitrate system.

$$Cu(NO_3)_2 \cdot N_2O_4 \rightleftharpoons Cu(NO_3)_2 + N_2O_4 \qquad \text{(reversible)}^{40}$$

$$Mg(NO_3)_2 \cdot N_2O_4 \longrightarrow Mg(NO_3)_2 + N_2O_4 \qquad \text{(irreversible)}^{12}$$

For the copper (II) nitrate system, the infrared spectra of both the adduct and nitrogen (IV) oxide-free compound indicate covalent bonding, but only the magnesium nitrate adduct has an infrared spectrum indicative of a covalent bond. The loss of a molecule of dinitrogen tetroxide results in a change to D_{3h} symmetry, and to an ionic substance. This same phenomenon is observed for the cobalt (II) nitrate system. Addison has suggested[41] that the irreversibility of the nitrate-adduct equilibrium is an indication of the ionic nature of the metal-oxygen bond. Cobalt (II) nitrate is interesting because it is one of the few nitrates that can be obtained as both a 1:1 and a 1:2 dinitrogen tetroxide adduct. The infrared spectrum of the 1:2 adduct has bands corresponding to the covalent nitrate group, the nitrogen (IV) oxide molecule, and the NO^+ group (at 2280 cm.$^{-1}$). However, after heating to obtain the 1:1 adduct, the bands due to loosely held dinitrogen tetroxide are gone. This has led Addison[41] to propose that the compound exists as $(NO^+)[Co(NO_3)_3]^-$, rather than as $Co(NO_3)_2 \cdot N_2O_4$. The 1:2 adduct would then be represented as $(NO^+)[Co(NO_3)_3] \cdot N_2O_4$, which is in accord with the ease of removal of one molecule of dinitrogen tetroxide from the 1:2 adduct to form the 1:1 adduct. The molecule of dinitrogen tetroxide cannot be removed from the 1:1 adduct by heating.

A similar situation exists with the anhydrous nitrate of iron (III). Both iron (III) nitrate and the 1:1 dinitrogen tetroxide adduct can be sublimed[13], indicating an unusual stability for the 1:1 adduct. Upon further investigation, Addison[42] discovered that the sublimed 1:1 adduct and the unsublimed 1:1 adduct had similar, but not identical infrared spectra. The unsublimed adduct had a strong band due to NO^+ in addition to bands from the covalent nitrate group, with no bands from dinitrogen tetroxide. From this he proposed that the adduct existed as $(NO^+)[Fe(NO_3)_4]^-$. The infrared spectrum of the sublimed compound still had bands corresponding to the strongly covalent nitrate group, but the NO^+ band had disappeared and in its place were two bands which he assigned to NO_2^+. This led him to propose that the sublimed nitrate existed as $(NO_2^+)[Fe(NO_3)_4]^-$. Conductivity measurements in non-aqueous solvents supported the presence of a 1:1 salt for both the sublimed and unsublimed products, and the equilibria,

$$N_2O_4 \rightleftharpoons NO^+ + NO_3^-$$

could not explain these conductivity studies.

The ultraviolet spectra for both compounds are very similar to that of $(Et_4N^+)[Fe(NO_3)_4]^-$ which again supports the existence of the $[Fe(NO_3)_4]^-$ group.

Addison also proposes a five-step mechanism for the conversion of NO^+ to NO_2^+ upon sublimation:

$$(1) \quad (NO^+)[Fe(NO_3)_4]^- \longrightarrow Fe(NO_3)_3 + 2NO_2$$

$$(2) \quad Fe(NO_3)_3 \longrightarrow Fe(NO_3)_2 + NO_3\cdot$$

$$(3) \quad Fe(NO_3)_2 \longrightarrow FeONO_3 + NO_2$$

$$(4) \quad NO_2 + NO_3 \longrightarrow N_2O_5$$

$$(5) \quad Fe(NO_3)_3 + N_2O_5 \longrightarrow (NO_2^+)[Fe(NO_3)_4]^-$$

The intermediate $Fe(NO_3)_2$ is not known, but $FeONO_3$ is known and can be prepared by allowing $Fe(NO)_5$ to react with nitrogen dioxide in the vapor phase. The infrared spectrum indicates that there are no ionic nitrate groups, no NO^+, and no NO_2 groups[43]. The mechanism proposed is involved, but it does account for the low yield of the product $(NO_2^+)[Fe(NO_3)_4]^-$.

Reactivity

The anhydrous metal nitrates are sufficiently reactive to attack sodium chloride infrared cells in many instances, causing the report of erroneous spectra due to the formation of the nitrate ion. It is the unusual reactivity of strongly covalent nitrates such as titanium (IV) nitrate, tin (IV) nitrate and zirconium (IV) nitrate which has attracted attention. It has been found that titanium (IV) nitrate reacts with hydrocarbons, such as Nujol to produce nitrates. This has led to the suggestion that the nitrate radical has been produced by the metal nitrate[34]. A similar phenomenon occurs with tin (IV) nitrate and zirconium (IV) nitrate, although the latter is much slower to react[8]. All three of these nitrates have bands above 1600 cm.$^{-1}$ in the infrared region, and it is probable that all three have bidentate structures, following the example of titanium (IV) nitrate[33]. Addison[8] suggests that this reactivity, due to the formation of the nitrate radical, can only occur when there are strongly covalent, bidentate nitrate groups involved and there is available a lower oxidation state. He describes the reaction for tin (IV) nitrate as:

$$Sn(NO_3)_4 \longrightarrow Sn(NO_3)_2 + 2NO_3.$$

The ease with which the metal ion can be reduced will then be a contributing factor to the ease of production of the nitrate radical. The order of increasing reactivity agrees well with the order of increasing ease of reduction.

$$\xleftarrow{\quad Sn \quad Ti \quad Zr \quad}$$

(increasing ease of reduction and reactivity)

Copper (II) nitrate has bidentate nitrate groups in the vapor phase, and it also has available a low oxidation state. The reactivity of gaseous copper nitrate with diethyl ether at room temperature is explained by Addison[8] by using this scheme. The inertness of solid α-copper nitrate is due to the absence of bidentate bonding in the molecule.

A similar phenomenon is observed with anhydrous chromium (III) nitrate, which reacts vigorously with ether, has a lower oxidation state available, and has a band above 1600 cm.$^{-1}$ in its infrared spectru, indicative of bidentate, covalent bonding. Further support for the idea that bidentate bonding is necessary for this reactivity comes from the fact that dimethyldinitrato tin (IV) is unreactive, whereas tin (IV) nitrate is extremely reactive. The infrared spectrum of dimethyldinitrato tin (IV) has no band above 1600 cm.$^{-1}$ [44], indicating that the nitrate group is no longer bidentate as it is in tin (IV) nitrate.

The reactivity of the nitrate group in the anhydrous metal nitrates is one more manifestation of the varied and surprising chemistry of what was once thought to be the nitrate ion, but which has been shown, in many instances to be an active, covalently bonded group.

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HETEROAROMATIC BORON COMPOUNDS

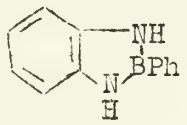
Fred R. Scholer March 31, 1966

Introduction

Chemists have known that atoms other than carbon can take part in conjugated systems and that heteroaromatic compounds of elements other than carbon exist. In recent years boron has become a respectable member of these heteroaromatic families. This seminar will deal with the advances in a specific field of boron-nitrogen chemistry, namely systems containing one adjacent boron and nitrogen atom. The interest in these derivatives was first stimulated when it was observed that they were stable to hydrolysis, a property which is not usually found in boron-nitrogen compounds.[1a,b,c,d,e,f,g,h]

Preparation

The first known organoboron compounds of this type were prepared by Ulmschneider and Goubeau.[1a] The 2-phenyl-2-boro-1,3-diazole (I) derivative was fairly stable in air and had a UV spectra similar to 2-phenylbenzimidazole rather than o-phenylenediammine. (Figure 1)



a) I

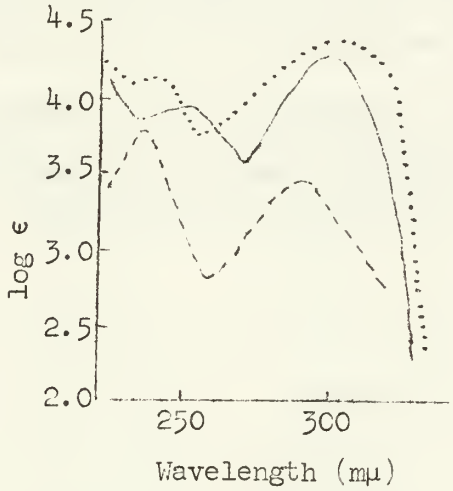
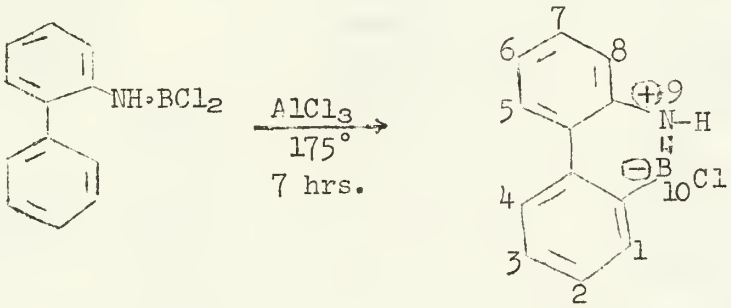


Fig. 1: a) I 2-phenylbenzo-2-bora-1-3-dizaole b) Ultraviolet spectra of 2-phenylbenzo-1:3:diaza-2-borole (—), 2-phenylbenziminazole (···), and o-phenylenediamine (---).

10:9-borazarophenanthrene (II) was first synthesized by Dewar, Petit, and Kubba.[2]



(1)

(II)

The UV spectra of 10:9-borazarophenanthrene also resembeled phenanthrene rather than the hindered diphenyl. (Fig. 2)

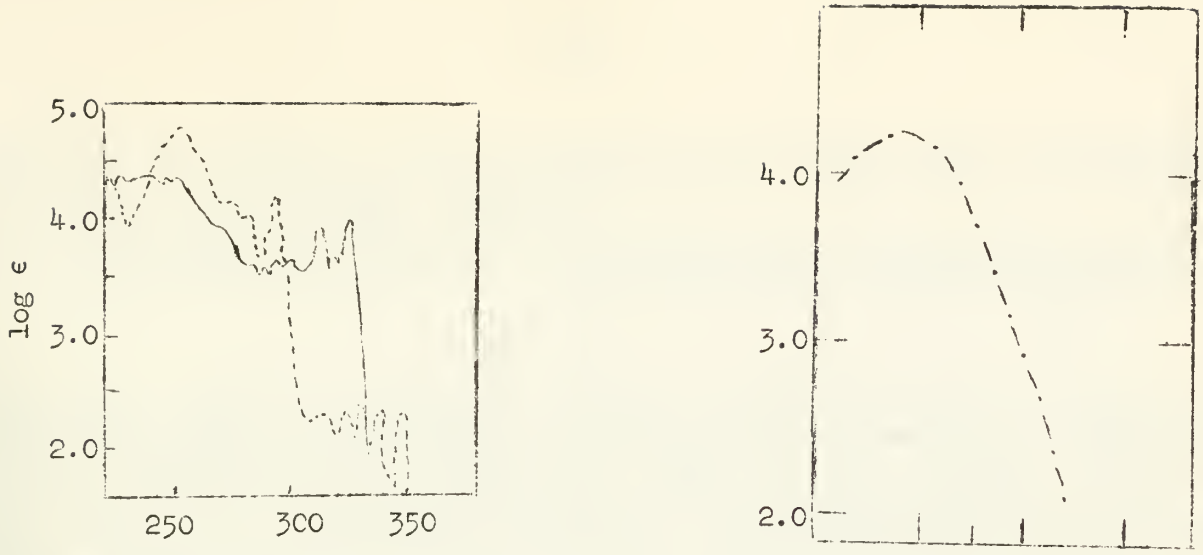


Fig. 2: Ultraviolet spectra of 10:9-borazarophenanthrene (—), and phenanthrene (---). Biphenyl (-·-·).

Molecular Orbital Applications

Both Dewar (1962) and Hoffman (1964) have obtained a qualitative set of numbers for the charge density and bond orders for 10:9-borazarophenanthrene.[3a,b] Because the use of data from charge transfer complexes has given consistent results with previous m.o. treatments of polycyclic aromatic hydrocarbons, Dewar decided to extend this treatment to 10:9-borazarophenanthrene derivatives.[4]

In order to use a Hückel treatment in the calculation of charge densities and bond orders, the coulomb integrals of boron and nitrogen and the BC and BN resonance integrals had to be determined. Figure 3 depicts both locally excited transitions and also the charge transfer transitions of electrons from donor A to acceptor B.

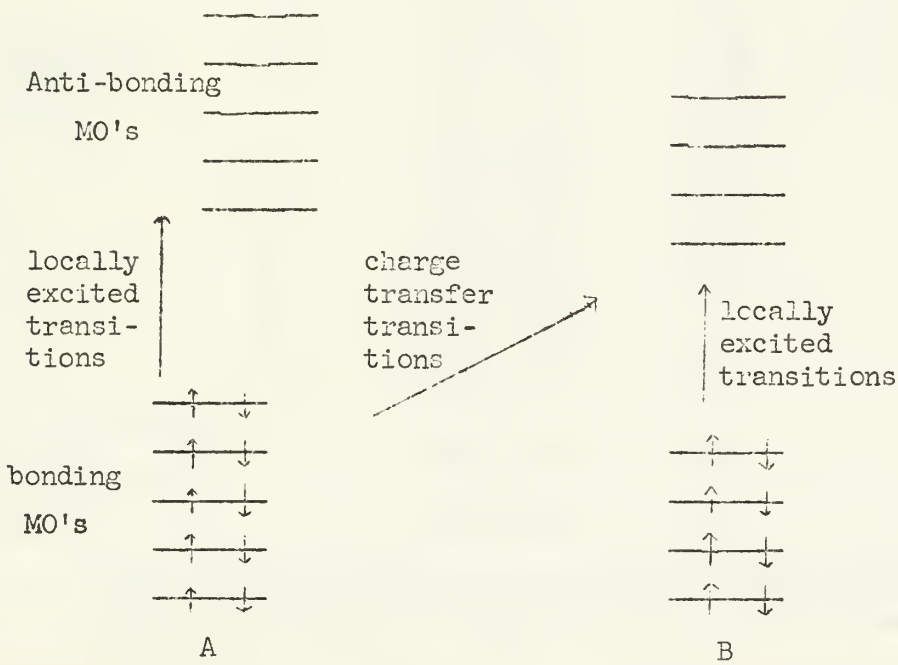


Fig. 3: Orbital energies and transitions in a molecular complex formed by a donor A and acceptor B.

The heats of formation of these complexes are at least an order of magnitude less than their lowest transition energies and are referred to as π-complexes rather than charge transfer complexes.

In the approach used by Dewar the energy of the charge transfer transition is represented by equation 2. B_j is the lowest unoccupied orbital on

$$\Delta E_{ij} = B_j - A_i \qquad (2)$$

the acceptor and A_i is the highest occupied orbital on the donor. In terms of simple m.o. theory the energies of the orbitals are of the form $(\alpha + \beta X)$; the relative energies therefore depend on βX, where β is the resonance integral and X is a theoretically calculated parameter of the orbital energies. If one plots ΔE_{ij}, vs X, a straight line results. This relationship holds quite well for the complexes formed by aromatic hydrocarbons with s-trinitrobenzene[4] and tetracyanoethylene.[3a]

The principle assumption in Dewar's proposal is that once this relation is established, the Hückel number X can be found for any other compound of this type by measuring the frequency of the charge transfer band of the π-complex. In Figure 4 a table of charge transfer spectra of s-trinitrobenzene and a plot of E_{ij} vs X is given.

TABLE 1

Compound	Symbol	Wave lengeth of charge transfer band, mμ	log ε	Calcd. energy of highest occupied MO
Benzene	1	284	..	1.000
Naphthalene	2	365	..	0.618
Acenaphthylene	3	353 ± 10	3.3	.637
Anthracene	4	460 ± 5	3.3	.414
Azulene	5	458 ± 5	3.0	.477
1,12-Benzoperylene	6	503 ± 10	3.23	.439
3,4-Benzotetraphene	7	490 ± 15	3.09	.405
1,2-Benzopyrene	8	464 ± 10	3.2	.497
3,4-Benzopyrene	9	480 ± 15	3.43	.371
Chrysene	10	430 ± 10	3.05	.520
Coronene	11	455 ± 10	3.47	.539
Naphthacene	12	520 ± 2	3.56	.294
Perylene	13	490 ± 15	3.42	.347
Phenanthrene	14	376 ± 5	3.1	.605
Picene	15	422 ± 30	..	.501
Pyrene	16	445 ± 5	2.84	.445
Triphenylene	17	384 ± 5	3.2	.684
10-Hydroxy-10,9-borazarophenanthrene		425 ± 10	2.9	...
10-Methyl-10,9-borazarophenanthrene		420 ± 10	2.7	...

Figure 4: a) Charge transfer spectra for hydrocarbon trinitrobenzene complexes and energies of highest occupied MO's of the hydrocarbons.

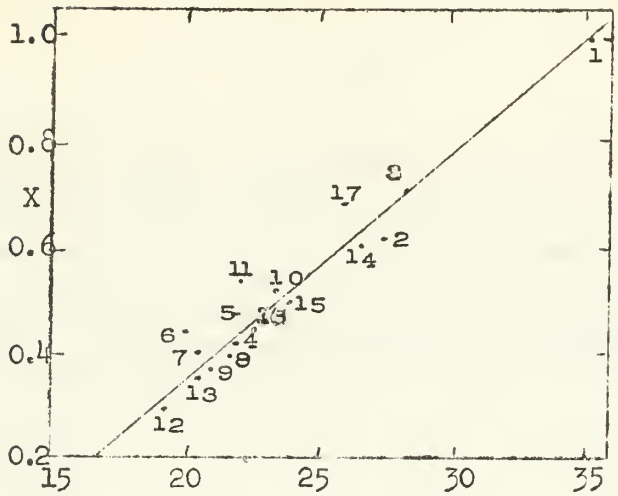


Figure 4: b) Plot of the frequencies (V) of the charge transfer bands of trinitrobenzene complexes against the molecular orbital parameter X.

The last column in Fig. 4, Table 1 lists energies calculated for the highest occupied orbitals given in terms of X. These values were obtained from the "Dictionary of Values of Molecular Constants."[5] The following treatment will give the method used for calculating the molecular parameters for boron. This method has also been extended to TCNE complexes.[3a]

As mentioned previously, the primary assumption is that the X values for the highest occupied m.o.'s 10:9-borazarophenanthrene derivatives may be obtained from the plot of Figure 4b. Using Figure 4b the following values were obtained. (Table 2)

TABLE 2

Compound	Energy of highest M.O.
10-hydroxy-10:9-borazarophenanthrene	$\alpha + .515\beta$
10-methyl-10:9-borazarophenanthrene	$\alpha + .525\beta$
phenanthrene	$\alpha + .605\beta$
borazarophenanthrene	$\alpha + .530\beta$

The value for borazarophenanthrene is extrapolated, because its s-trinitrobenzene complex decomposes. However the TCNE π-complex gives a value of $\alpha + .535\beta$.

The difference in values for phenanthrene and 10,9-borazarophenanthrene is represented by the equations 3 and 4 using the perturbation method of Longuet-Higgins.[6]

$$\delta E_1 = a_9^2(\alpha_C-\alpha_N) + a_{10}^2(\alpha_C-\alpha_B) \qquad (3)$$

$$\delta E_2 = a_9a_{10}(\beta_{BN}-\beta_{CC}) + a_9a_{14}(\beta_{CN}-\beta_{CC}) + a_{10}a_{11}(\beta_{BC}-\beta_{CC}) \qquad (4)$$

Equation 3 represents the over-all change in energy due to the difference in the electronegativity between carbon, boron and nitrogen. Equation 4 is the contribution due to the changes in the resonance integrals from phenanthrene to 10:9-borazarophenanthrene. Table 3 gives the values for the coefficients.[6]

TABLE 3

$$a_9 = a_{10} = .415$$
$$a_{11} = a_{14} = .164$$

The following approximations are made to reduce the variables.

$$\alpha_N - \alpha_C = \alpha_C - \alpha_B$$

$$\beta_{CN} = \beta_{BC}$$

Because the ionization potential difference between carbon and boron and nitrogen and carbon is small, equation 3 will equal 0. Also the second and third term in equation 4 will vanish. In figure 5 the energies of the highest occupied and lowest occupied orbitals of phenanthrene are, respectively, 0.605β and -.605β, corresponding to a transition energy of 1.21β. The experimental value is 1.21β. The experimental value of 10:9-borazarophenanthrene is 3.79 e.v., or 1.08β. Since we have determined the highest occupied orbital to be .53β, that of the lowest should be -0.55β.

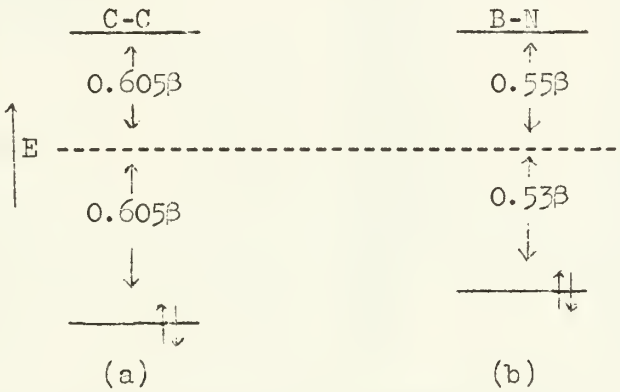


Figure 5: Energies of highest occupied and lowest occupied MO's for phenanthrene (a) and 10,9-borazarophenanthrene (b)

The center of gravity of the two orbitals for borazarophenanthrene is almost identical with that for phenanthrene. Therefore, any changes in the electronegativity of atoms in phenanthrene should alter the energies of both the highest occupied and lowest unoccupied orbitals in similar manner.

With these assumptions $dE_1=0$, and $dE_2=a_9a_{10}(\beta_{BN} - \beta_{CC})$

$$dE_2 = (0.415)^2(\beta_{BN} - \beta_{CC}) = -.075\beta$$

$$\therefore \beta_{BN} = \beta(1 - \frac{0.075}{(0.415)^2}) = 0.57\beta$$

The above value is based on an estimated value for the highest occupied m.o. for borazarophenanthrene. Although the number is reasonable Dewar repeated this work using π-complexes with TCNE instead of s-trinitrobenzene.[3a] This data is found in Table 3 and Figure 6.

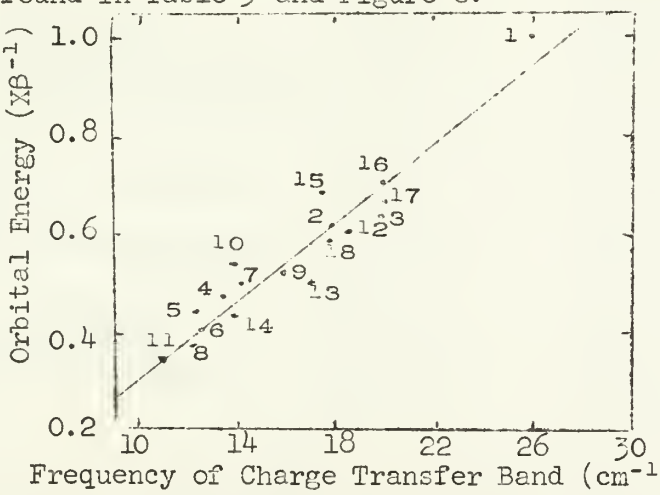


Figure 6: Plot of the transition energies of the charge transfer bands of hydrocarbon-tetracyanoethylene complexes against the energies of the highest occupied orbitals of the hydrocarbons; the points are numbered according to the code in Table 3.

TABLE 3a

Compound	Code number	Wave length of charge transfer band, mμ	Frequencies of charge transfer band (KK)	Energy of highest occupied MO ($X\beta^{-1}$)
Benzene	1	385 ± 2	26.0	1.000
Naphthalene	2	560 ± 5	17.8	0.618
Acenaphthylene	3	502 ± 5	19.9	.637
Azulene	4	740 ± 2	13.5	.477
1,12-Benzoperylene	5	812 ± 5	12.3	.439
3,4-Benzotetraphene	6	800 ± 5	12.5	.405
1,2-Benzopyrene	7	705 ± 2	14.2	.497
3,4-Benzopyrene	8	820 ± 2	12.2	.371
Chrysene	9	630 ± 2	15.9	.520
Coronene	10	725 ± 5	13.8	.539
Perylene	11	920 ± 5	10.9	.347
Phenanthrene	12	540 ± 2	18.5	.605
Picene	13	590 ± 2	16.9	.501
Pyrene	14	720 ± 2	13.9	.445
Triphenylene	15	570 ± 2	17.5	.684
Biphenyl	16	500	20.0	.704
m-Terphenyl	17	500	20.0	.662
p-Terphenyl	18	564	17.7	.592

Charge Transfer Bands of Complexes Formed By Polycyclic Aromatic Hydrocarbons with Tetracyanoethylene and the Hückel Energies of the Highest Occupied MO's of the Hydrocarbons

TABLE 3b

Compound	Wave length of charge transfer band, mμ	Frequency of charge transfer band X 10^{-3}	Energy of highest occupied MO from Fig. ($X\beta^{-1}$)
10,9-Borazarophenanthrene	633 ± 2	15.8	0.535
10-Methyl-10,9-borazarophenanthrene	605 ± 2	16.5	.56
10-Hydroxy-10,9-borazarophenanthrene	635 ± 2	15.7	.53
2,1-Borazaronaphthalene	475 ± 5	21.1	.75
1-Methyl-2,1-borazaronaphthalene	540 ± 2	18.5	.645
1-Phenyl-2,1-borazaronaphthalene	550 ± 5	18.3	.64
1-Methyl-3-chloro-2,1-borazaronaphthalene	515 ± 2	19.4	.68
2-Methyl-3-bromo-2,1-borazaronaphthalene	505 ± 2	19.8	.70
10-Hydroxy-10,9-boroxarophenanthrene	550 ± 2	18.3	.64
4,3-Dibromo-10,hydroxy-10,9-boroxarophenanthrene	470 ± 2	21.3	.76
10-Phenyl-10,9-boroxarophenanthrene	520 ± 2	19.2	.67

Charge Transfer Spectra of Complexes Formed By Various Heteroaromatic Boron Compounds with Triracyanoethylene and Derived Values for the Energies of Their Highest Occupied MO's

Using the same procedure he calculated β_{BN} and obtained a value of .59β. Since 5 parameters are needed, α_N, α_B, β_{CN}, β_{BC}, and β_{BN}, the previous assumption leaves only three independent quantities to be determined. In Table 4 are listed the values for the highest m.o.'s of four boron containing heteroaromatic compounds deduced from their spectra.

TABLE 4

Compound	Energy of Highest Occupied MO ($X\beta^{-1}$)
2,1-Borazaronaphthalene	0.75
10,9-Borazarophenanthrene	.535
2,7-Dibora-1,8-diazaroanthracene	.50
2,6-Dibora-1,7-diazaropyrene	.57

Comparison of the Energies of the Highest Occupied MO's of Four Boron-Containing Heteroaromatic Compounds Deduced From Spectral Data

Comparison of these values with equations 3 and 4 enables one to estimate the molecular orbitals parameters. All values of coefficients were obtained from "Dictionary of Molecular Constants."[6] Thus

$$\alpha_B = \alpha_C - 1.59\beta \qquad \alpha_N = \alpha_C + 1.59\beta$$

$$\beta_{CB} = \beta_{CN} = .9\beta$$

Dewar then used these parameters in a Hückel-type calculation to obtain the charge distributions, and bond orders (Figure 7).[7]

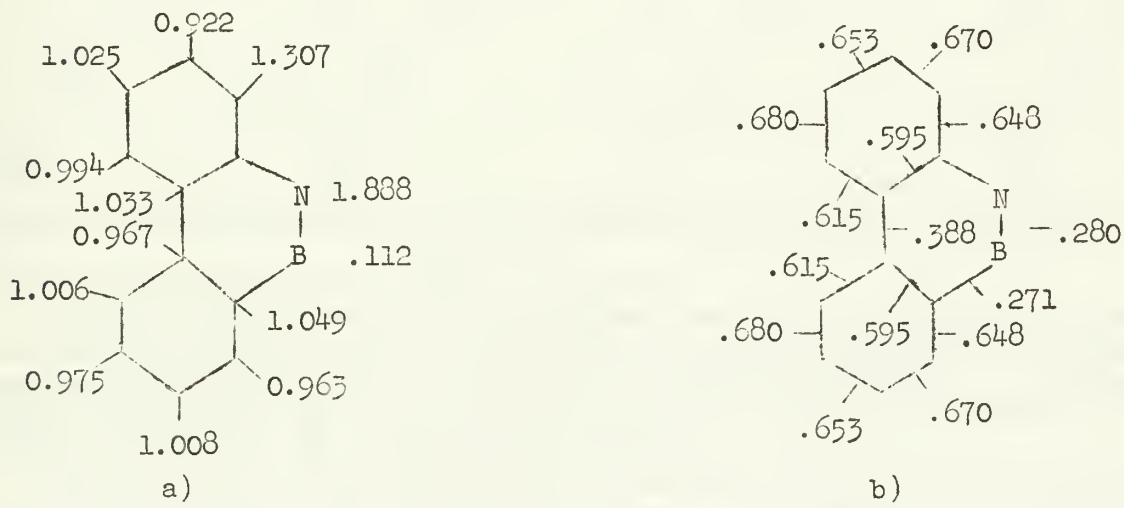


Figure 7: a) charge distributions of borazarophenanthrene
b) bond orders

Electrophilic Substitution

According to the data in Figure 7 the 6-8 positions should be most susceptible to electrophilic attack followed closely by the 3 position. There has been extensive work done in the areas of nitration[8], chlorination and bromination[9] and Friedel-Crafts acetylation[10] of 10,9-borazarophenanthrene. In Table 5 is a list of the proportions of isomers formed in each reaction.

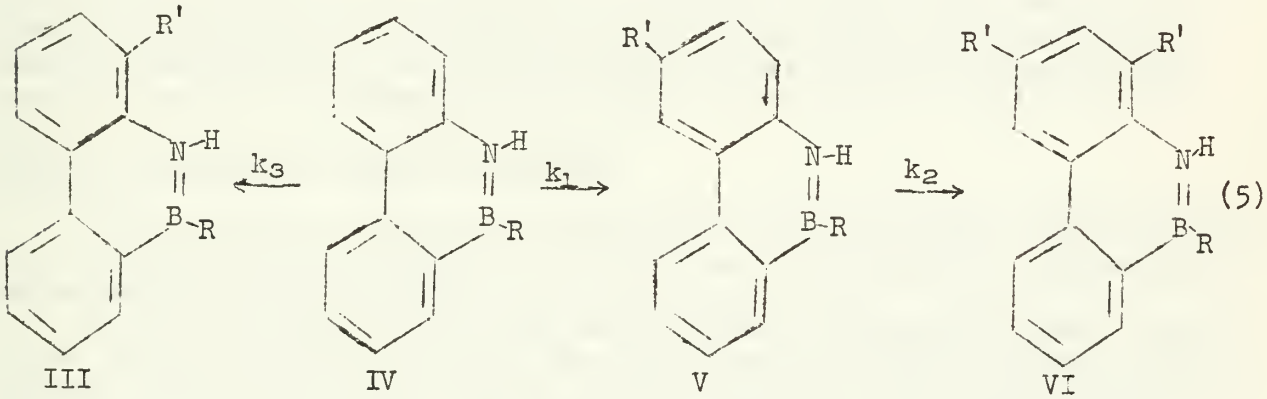
TABLE 5

Proportions of Isomers In Substitution Reaction of Borazarophenanthrene Derivatives

Reaction	6-substitution	8-substitution	6,8-substitution
Chlorination of (II R = Me)	0	100	0
Nitration of (II R = Me)	34	66	0
Nitration of (II R = OH)	33.5	66.5	0
Acetylation	42.4	0	17.4

The derivatives are unchanged by boiling with alkali or concentrated hydrochloric acid, but could be degraded to derivatives of 2-aminodiphenyl by cold concentrated sulfuric acid.

In agreement with the calculations above, the 6 and 8 isomers are formed exclusively. However vigorous conditions of chlorination has given the 2,6,8-trichloroderivative. The unusual result in the acetylation reaction is explained by the formation of a deactivated complex 10,9-borazarophenanthrene and $AlCl_3$. This complex is less reactive than the 6-acetyl-10,9-borazarophenanthrene derivative. This system is depicted in equation 5.

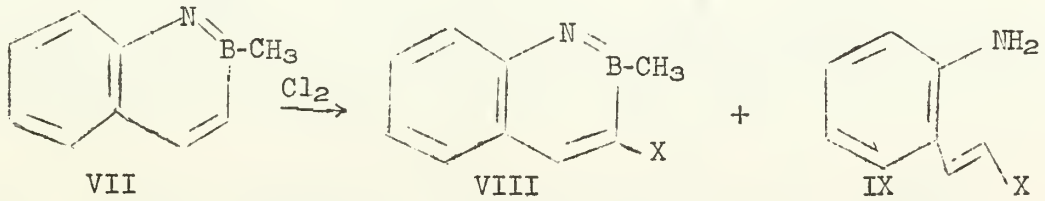


(5)

Rates of Acetylation for 10-9 borazarophenanthrene versus 6-acetyl-10:9-borazarophenanthrene ($R' = CH_3\overset{O}{\overset{\|}{C}}-$) ($R = OH^-$).

$k_1 > k_2 \gg k_3$ because the $AlCl_3$ complex does not form readily with the less basic nitrogen of the 6 acetyl-derivative (V) and thus reacts faster than the $AlCl_3$ complex of 10-hydroxy-10:9-borazarophenanthrene. Consequently further acetylation of the monoacetyl derivative competes favorably with the initial acetylation of the starting material.

All this data on electrophilic substitution does not require that the central ring be part of a conjugated system. If the central ring did not have aromatic character, the same distribution of isomers would probably be obtained since mesomeric effects would activate positions ortho and para to the nitrogen. In an attempt to solve this problem similar chlorination experiments were tried on 2:1-borazaronapthalene. The following derivatives were obtained (equation 6).



(6)

Dewar has proposed the following intermediate for the electrophilic reaction in Figure 8.

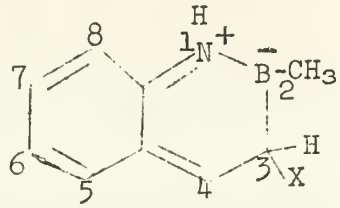


Figure 8: Intermediate in electrophilic substitution of 2:1-borazaronapthalene.

However calculation of charge densities would predict the 6 and 8 isomer as products.[10] In both the 10:9-borazarophenanthrene and 2:1-borazaronapthalene the isomer distribution does not correspond to the calculated values, but rather at the points of maximum π-electron density.[7]

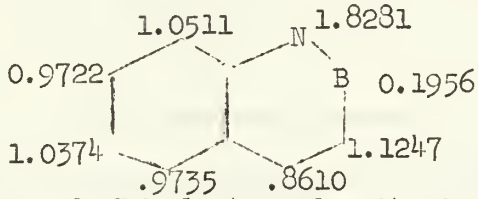


Figure 9: Distribution of π-electron density in 2:1-borazaronapthalene.

Dewar believes that this evidence should shed new light on the area of π-complexes formed during electrophilic substitution. The data obtained from electrophilic reactions does not conclusively prove that the boron-nitrogen couple is part of an aromatic ring system.

Further Evidence for Aromatic Character

In the previous reactions and compilation of data aromatic like properties are indicated by the substitution reactions and the resistance to hydrolysis and oxidation of the B-N bonds.

A series of chemical reactions were designed to determine whether there is any resonance stabilization of the central ring of 10,9-borazarophenanthrene At first the situation was slightly confused when R. Huisgen determined the dipole moment of 10-9 borazarophenanthrene and obtained a very low dipole moment of .16 ± .021D.[12] A larger number was expected due to the dipolar structure for the ground state of the molecule. Also a stable cyclic boron derivative was prepared by Snyder in 1958 and '59 which could suggest that the stability of 10:9-borazarophenanthrene is due to its cyclic structure and not any resonance effects.[13,14]

The first piece of data used by Dewar to support his theory was the synthesis of borazarophenanthrene derivatives with +E substituents on the nitrogen, such as a carbethoxy group, or a -E substituent on boron[15] (Figure 10).

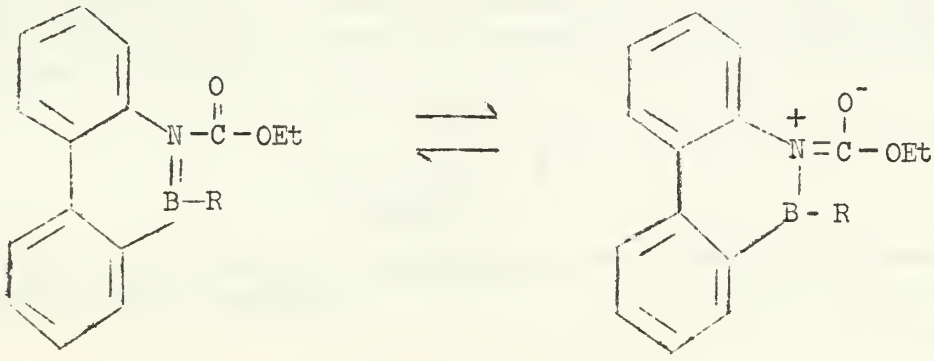


Figure 10: Resonance structure of carbethoxy derivative (R = alkyl)

Such electron withdrawing substituents attached to the nitrogen reduce the resonance stabilization of the central ring, and should lead to a decrease in the stability. The isolated product oxidized rapidly in the air and no longer contained a maximum at 320 mμ typical of borazarophenanthrene.

Second, if the nitrogen is exchanged for an oxygen, we would expect the B-O analog to be less stable. The $-RB^{-}=O^{+}R$ contributes less to the overall resonance model than $RN^{+}=B^{-}R$.

Third, if the stabilization were only due to the cyclic structure, then 10,9-borazaroanthracene (Figure 11) should show a stability equal to that of borazarophenanthrene.[16]

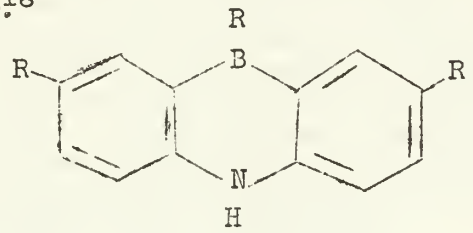


Figure 11: 10:9-borazaroanthracene (R = methyl)

The boron and nitrogen are still incorporated in a ring and should be stable if resonance effects are minor. In alcoholic potassium hydroxide there is a large bathochromic shift, while in 10:9-borazarophenanthrene the shift is minor. This is explained by the expansion of the coordination number of boron from 3 to 4 in the basic solution and loss of any delocalization in central ring.

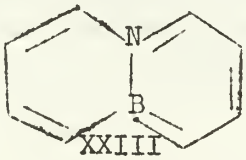
NQR studies on pyridine, which show a large difference in conjugative interaction between 4 chloropyridine and 2-chloropyridine, suggest this could be extended to borazarophenanthrene.[17]

NMR Spectra

Dewar has spent a large amount of time on the synthesis and characterization of fluorine aromatic compounds. Since the chemical shifts shown by the fluorine n.m.r. seem to reflect the π-electron density of the ring atom adjacent to the fluorine, this may be used as a check on the M.O. treatment.[13] However the synthesis of the various fluorine isomers of borazarophenanthrene is quite a challenge. At this time only the 2,3,6 and 7 isomers have been isolated.[19] As of this time no work has been published on the F^{19} n.m.r. of borazarophenanthrene, although there has been numerous reports on the F^{19} n.m.r. of aromatic hydrocarbon.[20]

It has been determined that the introduction of a substituent shifts the fluorine resonance by an amount and direction characteristic of the substituent and its position in the molecule. Dewar has suggested that the fluorine n.m.r. is in line with the current treatments of borazarophenanthrene.[20]

The only complete and detailed analysis of the n.m.r. of a B-N heteroaromatic is that of 9,10-borazaronapthalene. This is isoelectronic with napthalene but contains no boron free aromatic rings as in 10,9-borazarophenanthrene.[21] (XXIII)



XXIII

The structure of the saturated intermediate was proven by its mass spectrum and also its n.m.r. spectrum.

There is found a ratio of peaks 1:2:1 at 7.1, 8.5, and 9.1 τ respectively. The peak at lower field corresponds to methylene adjacent to nitrogen and the peak at high field to a methylene adjacent to boron.

10,9-borazaronapthalene consists of a well defined doublet centered at 2.28 τ, a well defined quartet at 3.36 τ, and lines in the region 2.5 - 2.8 τ that is interpreted as a doublet centered at 2.67 τ and a quartet at 2.53 τ. Any inductive effects of the nitrogen and boron causing a shift to the aromatic would have to be discounted as being too small. Normal inductive effects like this are not usually felt over two carbon atoms.[22]

The low field doublet at 2.28 τ is clearly assigned to the 1,8 protons adjacent to the electronegative nitrogen rather than boron. The doublet at 2.67 τ is then assigned to the 4 and 5 positions. At the present all theories suggest higher π-electron density at the 2 and 7 positions rather than the 3 and 6. Therefore the quartet at high field (3.36 τ) is assigned to the 2 and 7 positions. The remaining quartet at 2.53 τ is assigned to the 3 and 6 position. The coupling constants for pairs of vicinal protons are consistent with the previously mentioned assignments.

$$J_{12} = 6.5$$

$$J_{23} = 6.0$$

$$J_{34} = 10.0$$

Thus the probable order of the π electron densities would be 2,7 >>1,8> 4,5 ~3,6 if the afore mentioned assignments are accepted. The signals for protons α to boron are shifted upfield relative to those α to nitrogen by approximately 2 τ due to the inductive effects of boron and nitrogen in the saturated system. In the aromatic derivative the difference is much less (.39 τ). To account for this smaller difference involved in the inductive effect, it would seem clear that the π electron density at the 1 and 8 positions must be greater than in the 2 and 7 positions.

The calculated π electron densities are given in Table 6.

TABLE 6

Calculated Electron Densities In 10,9-Borazarophenanthrene

Position	Perturbational[7] MO	Hückel MO	SCF-MO[23] PPP	SCF-MO[24] SPO
1	0.907	0.953	0.985	0.994
2	1.056	1.022	1.022	1.016
3	0.994	0.969	0.951	0.962
4	1.093	1.052	0.971	0.956

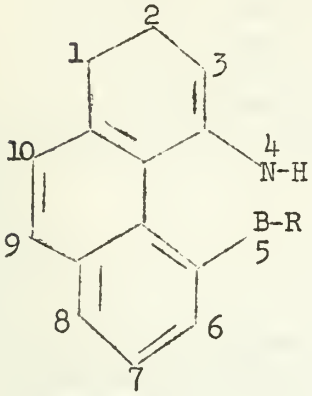
According to the n.m.r. theory the π electron density follows in the decreasing order 2 >1 >4 >3. Only the two SCF-MO treatments lead to the predicted results. Previous theoretical treatments concerning conjugated systems containing heteroatoms have admittedly been fairly crude and by no means quantitative. Dewar believes that a semi-empirical SCF-MO treatment may prove more successful.

Novel B-N Derivatives

The synthesis and characterization by borazarophenanthrene has led to the production of many interesting boron-nitrogen heterocyclics. These new deriva-

tives can be separated into three major categories: Class I are the boron-nitrogen analogs of polyaromatic systems, Class II are boron-nitrogen analogs of polyaromatic systems with either a boron or nitrogen at a bridgehead and Class III consists of six membered rings containing a boron-nitrogen couple.

In Class I the following types have been isolated.



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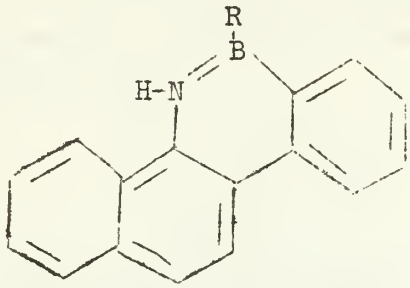

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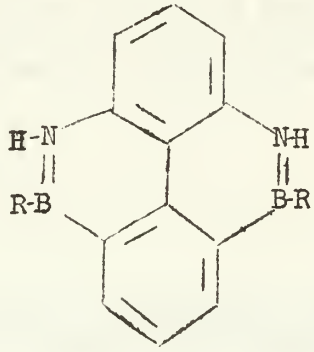
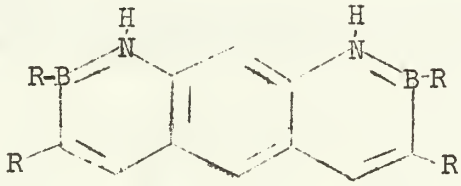


III



IV

Figure 12: Examples of Class I Compounds.

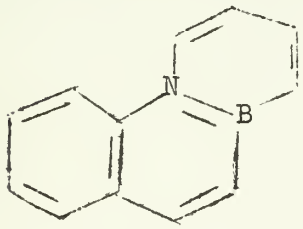
(I) 5:4-borazaropyrene (R = Cl, OCH_3, Me, H) is closely analogous to its parent carcinogenic hydrocarbon.[25] Using the method described previously (I) may be used for a check of quantum mechanical theories of molecular structure.

(II) 6:5-borazarochrysene (R = Cl, OCH_3, Me) is similar to (I) but the UV and charge transfer peaks are shifted to longer wave length.[25]

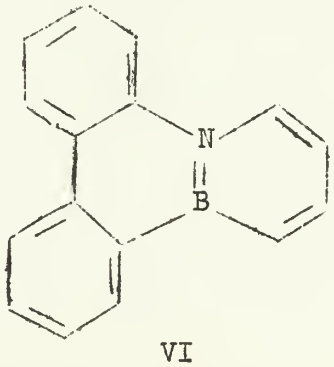
(III) 4:10-dibora-5:9-diazopyrene, the 9 bora-10-aza analog of I, has been condensed by the usual Friedel-Craft synthesis.[26] A novel attempt to isolate the 4:9-dibora-5:10-diazapyrene isomer failed due to the deactivating effect of the quaternary nitrogen.

In an extension of dibora-diaza adducts 2:7-dibora-1:8-diazaanthracenes (R = ∅) IV has been isolated.[26]

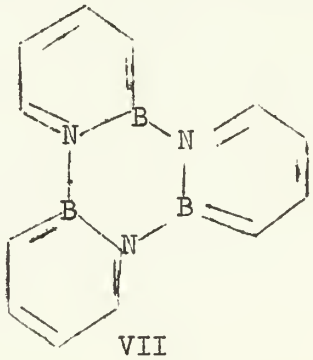
In Class II the first heteroaromatic compound containing bridgehead borons or nitrogens was 12-11-borazarophenanthrene V.[27] The synthesis of these derivatives is a good example of the ease of nucleophilic displacement on boron. In V MeMgBr is split off in the process of cyclization. Analogs of triphenylene,



V



VI

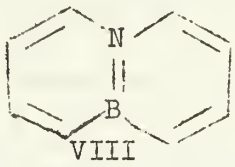


VII

Figure 13: Examples of Class II Compounds.

VI - 14-13,borazarotriphenylene and 14,16,18-tribora-13,15,16-triazarotriphenylene VII have been prepared.[28] They are both novel and interesting. VI is an excellent example of the stability of these systems. Borazarotriphenylene was stable in strong acid or base, but also did not undergo any Diel-Alder additions with moleic anhydride as anthracene would. This indicates the outer ring is highly stabilized. Triboratriazarophenylene undergoes hydrolysis quite easily and appears to be a source of the borazarene family.

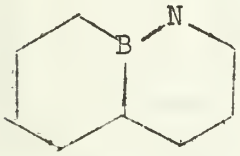
The synthesis of 10:9-borazaronapthalene VIII is of great significance for it represents the only example of a heteroaromatic compound, where all rings contain a boron atom.[21]

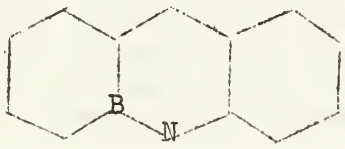


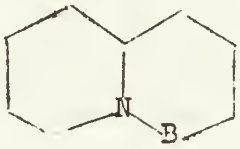
VIII

This derivative has already been used for n.m.r. studies and would be of further interest in the areas of arene complexes, contact shift studies, and epr studies of radicals.

The field of boron-nitrogen aromatics is still wide open. Hoffman has proposed the following compounds as being stable and possible to synthesize.[3b]







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SOME APPLICATIONS OF INORGANIC PHOTOCHEMISTRY

David Hyatt April 19, 1966

Introduction

Recent interest in the field of photochemistry has been largely directed toward research into organic photochemical reactions. A recent review article[1] on this subject devotes only four pages to inorganic photochemical reactions. It is the purpose of this seminar to discuss some of the recent advances in inorganic photochemistry which have appeared in increasing numbers in the past few years. Before discussing specific examples it is best to review some of the fundamentals of photochemistry.

Fundamentals of Photochemistry

The basic requirement of photochemistry is that one have a species capable of activation to a reactive state by photolytic means. Figure 1 represents the basic occurances following irradiation which may be termed photophysical phenomena, while Figure 2 presents a compilation of some of the possible chemical routes to deactivation of the excited state.

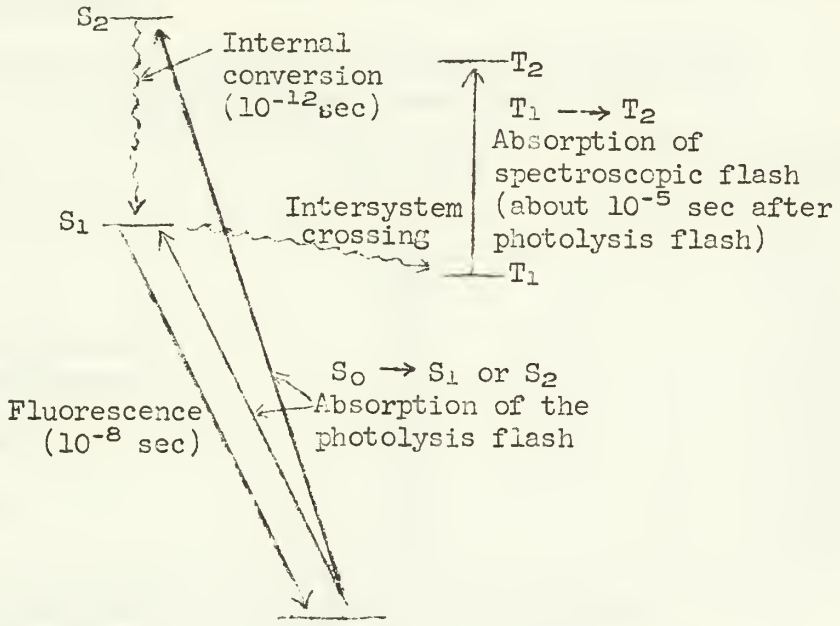


Figure 1

$A + h\nu \rightarrow {}^1A$	1
${}^1A \rightarrow A + h\nu'$	2
${}^1A \rightarrow {}^3A$	3
${}^1A \rightarrow A$	4
${}^1A + A \rightarrow {}^1AA$	5
${}^1AA + A \rightarrow {}^1A + A_2$ (or $A + A$)	6
${}^1AA \rightarrow A + A$	7
${}^1AA \rightarrow A_2$	8
${}^1AA \rightarrow A + A + h\nu''$	9
${}^1A + {}^3O_2 \rightarrow {}^3A + {}^1O_2$	10
${}^3A + {}^3O_2 \rightarrow AOO$	11
$AOO \rightarrow A + O_2$	12
$AOO + A \rightarrow A + AO_2$	13
${}^3A \rightarrow A + h\nu'''$	14
${}^3A \rightarrow A$	15

A = ground, ${}^1A$ = excited singlet, ${}^3A$ = triplet states of hydrocarbon molecule; A_2 = stable dimer, AO_2 = cyclic peroxide; ${}^1AA$ and AOO represent intermediates.

Figure 2

The reactive state responsible for the majority of photochemical reactions has been shown to be the lowest vibrational state of the first excited singlet (S_1) or triplet (T_1) levels. Therefore for this discussion, we will consider this to be the reactive state (S) most reasonably encountered. A detailed discussion of the methods employed to determine the actual character of the excited state will not be undertaken here, but later, mention and discussion of flash photolysis experiments with $Ni(CO)_4$ will touch upon one of the more popular methods. The topic of flash photolysis itself has been quite extensively reviewed and a recent seminar discusses some specific applications of this analytical method.[2]

The photophysical pathways to deactivation of the S_1 or T_1 states differ mainly in the lifetime of the activated species prior to fluorescence or phosphorescence. In general, it is found that the phosphorescence from $T_1 \rightarrow S_0$ occurs a longer time after activation than does fluorescence from $S_1 \rightarrow S_0$ and consequently the triplet species have longer lifetimes and higher probabilities of reacting than do the excited singlet states. Studies on systems containing T_1 states show that such states are highly populated in solution as well as in low temperature glasses,[3] and that conversion of $T_1 \rightarrow S_0$ is slower than $S_1 \rightarrow S_0$ transitions by a factor of 10^3 to 10^6. Figures 3 and 4 list some of the lifetimes of excited singlet and triplet states prior to $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ transitions for some of the more common organic systems studied.

Experimental and Calculated Lifetimes in Seconds for Singlet-Singlet Transitions

Compound	τ (X 10^9)[a]	τ (X 10^9)[b]
Rubrene	22.0	16.0
Anthracene	13.5	16.7
Perylene	5.1	5.6
9,10-Diphenylanthracene	8.9	8.8
9,10-Dichloroanthracene	11.0	15.4
Acridone	15.9	15.1
Quinine sulfate[c]	27	3.6
Fluorescein	4.7	5.0
9-Aminoacridine	15.6	15.3
Rhodamine B	6.0	6.0

[a] Calculated from singlet-singlet absorption spectrum.
[b] Measured experimentally from observed τ_f and ϕ_f.
[c] Acid-base reactions may cause this compound to be peculiar.

Figure 3

Experimental and Calculated Lifetimes in Seconds for Triplet-Singlet Transitions

Compound	τ (X 10^3)[a]	τ (X 10^3)[b]
Anthracene	90.0	0.1
1,4-Dibromobenzene	1.5	0.3
1,3,5-Tribromobenzene	1.2	0.7
1,2,4,5-Tetrabromobenzene	0.6	0.5
Bromobenzene	3.0	1.0
Chlorobenzene	6.0	4.0
2-Bromonaphthalene	10.0	20.0
2-Iodonaphthalene	2.0	3.0

[a] Calculated from singlet-triplet absorption measurements.
[b] Measured experimentally from lifetime and quantum yield data.

Figure 4

Turning from the process of photophysical deactivation to photochemical deactivation, one finds an increase in the number of pathways which appears at first overwhelming. It is, however, possible to eliminate reaction with O_2, abstraction of protons from solvents, dimerization (to a lesser degree) and similar side reactions by proper choice of reaction conditions in many cases. The problems of side reactions from photoactivation of products, however, is not so easily overcome and consequently may complicate studies. In some cases it may be possible to utilize these side reactions, but in the present discussion we will assign no role to them and will concern ourselves only with the reactions of the excited S_1 or T_1 states and the species derived from them.

Concluding the general discussion of photochemical basics, we may cite some requirements for a photochemical reaction: (1) A species capable of the absorption of the available wavelengths of light must be present. The use of activating or sensitizing species such as mercury may allow activation of species which themselves will not absorb light of the available frequency. (2) The lifetime of reactive intermediates must be long enough to allow photochemical reaction prior to photophysical deactivation. (3) Suitable reaction conditions must be chosen to prevent reactions with O_2, proton abstraction from solvent, and similar side reactions. Figure 5 lists some of the common u.v. chromophoric groups and the region in which they absorb; the bulk of the remaining discussion will deal with the reactions of carbonyl compounds, one of the most often studied class of compounds in photochemical reactions.

Chromophore	Absorption Region (mμ)
C=C	190
C≡C	170
C=O	190,280
N=N	350
N=O	300
Aromatics	250-300

Figure 5

Metal Carbonyl Reactions

The photochemical reactions of carbonyl compounds has been rather extensively studied in the field of organic chemistry[4] and a similar situation exists in the field of inorganic photochemistry. Strohmeier and others have studied rather extensively the reactions of substituted and unsubstituted metal carbonyls with basic ligands; Figure 6 lists some of the species studied and the recent paper on this topic may be referred to for further details.[5]

Parent Molecule	Substituted Species	
$Cr(CO)_6$	$C_6H_6Cr(CO)_3$	$(CH_3)_3C_6H_3Cr(CO)_3$
$W(CO)_6$	$C_5H_5Mn(CO)_3$	
$Mo(CO)_6$	$C_5H_5V(CO)_4$	
$Mn_2(CO)_{10}$	$C_5H_5Rh(CO)_2$	
$Fe(CO)_5$	$C_5H_5Co(CO)_2$	
$Co_2(CO)_8$	$[C_5H_5Cr(CO)_3]_2$	
$Os_3(CO)_{12}$		
$Mn(CO)_5^-$		

Figure 6

The reactions of $Mn_2(CO)_{10}$ and $C_5H_5Mn(CO)_3$ with trialkyl phosphines are found to lead to diamagnetic substitution products of the form $[Mn(CO)_4R_3P]_2$ which are not isolated from thermal reactions where paramagnetic monomers are the products.[24] This observation illustrates the utility of photolytic reactions in providing more selective activation than is usually possible with thermal reactions. The preparation of $W(CO)_5(CH_3CN)$ and $W(CO)_4(CH_3CN)_2$ as well as $W(CO)_3(CH_3CN)_3$ from the reaction of $W(CO)_6$ with CH_3CN under photolysis conditions[27,10] also illustrates this enhanced selectivity since thermal reaction yields the trisubstituted product.[28] The reaction of $C_5H_5V(CO)_4$ with ethylene and substituted acetylenes under photolytic activation using a mercury sensitizer is reported[5] to yield compounds of the type $C_5H_5V(CO)_3R$ which have not been obtained under thermal reaction conditions. The thermal substitution of CO groups in $Fe(CO)_5$ using PF_3 is reported to give only small yields of $Fe(PF_3)_5$ due to extensive decomposition, but photochemical substitution is reported to yield members of the series $Fe(CO)_{5-x}(PF_3)_x$ with little decomposition and in controllable ratios.[7] A similar reaction with $Ni(CO)_4$ is reported not to yield the compound $Ni(PF_3)_4$.[6] The foregoing reactions are only a partial listing of reactions in which photolytic conditions yield products not obtained under thermal conditions; references to other systems may be found in some recent reviews.[30]

Although a large majority of the photolytic reactions of metal carbonyls studied have been substitution reactions, some coupling reactions have been studied. The photolysis of $Fe(CO)_5$ yields fairly large yields of the dinuclear carbonyl $Fe_2(CO)_9$.[7a] The photolytic decarbonylation of $R_fCOM(CO)_x$ proceeds in a manner similar to the thermal decarbonylation to yield the perfluoro alkyl derivative $R_fM(CO)_x$.[26] A somewhat more subtle transformation by photolytic activation is the synthesis of π-$C_3H_5W(CO)_3C_5H_5$ by irradiation of σ-$C_3H_5W(CO)_3C_5H_5$.[11] The preparation of anionic species of the type $Fe(CO)_4^-$ and $Fe_2(CO)_8^-$ may be accomplished by the photolysis of $Fe(CO)_5$ in dimethyl sulfoxide.[29]

Having reviewed to this point some of the synthetic applications of photochemistry in inorganic systems, it is interesting to look briefly at some of the kinetics studies made possible, or at least less complex, by photochemical activation procedures.

Mechanism and Kinetics Studies

A very useful advance in the determination of the mechanism of a reaction is the identification of intermediates, and photolytic reaction conditions often provide a means for such identifications. Two mechanistic studies will be discussed here: (1) the flash photolysis study of the reactive intermediates of $Ni(CO)_4$ and (2) the use of low temperature "glass" irradiation to produce intermediates of Group VI hexacarbonyls which were then studied by infrared and ultraviolet spectrophotometry. The latter study, in addition to providing mechanistic details of substitution reactions, was in part useful in explaining the mechanism of catalysis by metal hexacarbonyls in the polymerization of some olefins.[12]

Early studies[13] into the mechanism of thermal decomposition of $Ni(CO)_4$ led to a proposed mechanism based on experiments in which solid product formation produced a heterogenous phase thus complicating the reaction system. A more recent study of this reaction utilized conventional flash photolysis apparatus to give what appears to be more meaningful results.[14] Employing spectroscopic flashes at varying intervals after the initiating flash

(itself varying in intensity from 500 to 1000 joules) and using high pressures of inert gas, the course of an essentially isothermal reaction could be followed. The findings of this experiment led to a decomposition pathway summarized in Figure 7.

<u>Photolytic Decomposition</u>

$$Ni(CO)_4 + h\nu \rightarrow Ni(CO)_4^*$$

$$Ni(CO)_4^* \rightarrow Ni(CO)_3 + CO$$

$$Ni(CO)_3 + h\nu' \rightarrow Ni(CO)_2 + CO$$

$$2Ni(CO)_2 \rightarrow \text{Solid Products}$$

Figure 7

If one compares these results with those from thermal degradation studies, the stability of the postulated $Ni(CO)_3$ intermediate is further substantiated by the observation that solid products are observed only after decomposition of $Ni(CO)_3$ to $Ni(CO)_2$. The thermal kinetic data suggest direct decomposition of $Ni(CO)_3$ to solid products of Ni and CO; a conclusion invalidated by the absence of atomic nickel lines in the spectra during photolytic decomposition.

One may of course argue that photolytic decomposition pathways and thermal pathways need not agree due to the heterogeneity of the thermal reaction, but at the same time the utility of flash photolysis in this system cannot be ignored. The flash photolysis method not only allows the detection of short lived intermediates but may also provide simultaneous information on the behavior of these species (lifetimes, relative concentrations, character of excited state, and so forth) providing a basis for predictive chemistry on the system.

The study of the reaction intermediates of metal hexacarbonyls was prompted by earlier postulates that the reactive intermediate in displacement reactions was a pentacoordinated species $M(CO)_5$.[15] The problems of thermal generation of this species in relatively high concentrations made its study difficult, but the observed photochromism of $Cr(CO)_6$, $W(CO)_6$, and $Mo(CO)_6$ in low temperature glasses[16] led to studies which confirmed the species produced by irradiation to be $M(CO)_5$ as postulated. Irradiation of isopentane-ether glasses of the hexacarbonyls at 77°K with u.v. irradiation followed by warming allowed infrared identification of species having the predicted symmetry for $M(CO)_5$. $Cr(CO)_5$ and $W(CO)_5$ were postulated to be of C_{4v} symmetry (having three I.R. active carbonyl bands)[18] while $Mo(CO)_5$ was found to be C_{4v} at temperatures below -155°C and D_{3h} at temperatures above -155°C. The lack of any esr signal has been offered as proof that the reactive intermediate is not a negative ion radical, and this, in conjunction with the symmetry requirements of the infrared spectra, supports a pentacoordinated square pyramidal species with an unoccupied orbital acting as acceptor for basic ligands.

In addition to allowing the generation of higher concentrations of $M(CO)_5$ species, the use of low temperature irradiation has allowed approximation of the lifetime of this species, and a value of about 2 minutes has been reported.[17] The utility of flash photolysis conditions, with its range of isothermal activation conditions and its ability to detect short lived intermediates at higher temperatures would be of real benefit here, but no such studies are reported to date.

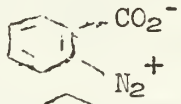
Before concluding this portion of this seminar, it should be mentioned that photolytic decomposition of solids has also been used in studying the mechanism of such decomposition. A recent report[31] on the photochemical decomposition of NaN_3 in the solid state provides a reference for such a system. The decomposition of organic azides has also been studied under photolysis conditions[32], but for reasons other than those underlying the study with NaN_3 which is a good source of high purity metallic Na upon decomposition.

Miscellaneous Photo-Reactions

Before concluding, it is of value to review briefly some of the reported work in photochemistry other than that involving the metal carbonyls already discussed. Photochemically induced racemizations, aquations, ligand exchanges, oxidations and reductions have been noted for a number of Cr(III), Co(III), Mo(IV), and Pt(IV) complexes in which ligands such as oxalate or halogens are the coordinating groups.[19,20] In a few cases, it appears that photoinduced racemization occurs by irradiation at ligand absorption frequencies while photoreduction or oxidation occurs upon irradiation at a charge transfer band,[19] but this observation does not appear to be widely enough applicable to serve as a general synthetic tool.

The photolytic cleavage of Mn-Mn bonds has already been noted in the reaction of $Mn_2(CO)_{10}$ and recently other reactions involving metal-metalloid bond cleavage have been studied.[21] The reaction of $(R_3Si)_2Hg$ and $(R_3Ge)_2Hg$ under photolytic conditions is found to produce products with Si-Si and Ge-Ge bonds and intermediary R_3Si and R_2Ge free radicals are postulated intermediates. While no reference was found for photolytic cleavage of Sn-Sn or Pb-Pb bonds, it may be postulated that such cleavages may be photolytically induced thus producing reactive intermediates similar to the silyl and germyl cases. Another potentially interesting source of reactive intermediates is S_2Cl_2 which is reported[23] to undergo photochemical degradation to species such as SCl, S_2, and S_2Cl. These latter species may possibly serve as intermediates capable of insertion reactions similar to those of SO_2.

Speculation on Interesting Systems

The number of potentially interesting systems capable of being obtained by photolysis of organic substrates is clearly too large to discuss at length here, but there are two systems recently studied which do present the possibility of producing novel ligands. The photolysis of  is reported[22] to yield fairly high percentages of a reactive species  , benzyne, whose lifetime prior to coupling may be long enough to allow reaction with metal carbonyls or similar species. The possibility of σ bonded aryl derivatives, π bonded arene derivatives, and/or π bonded acetylene like derivatives may be postulated, and perhaps even combinations of these bonding systems not observed prior to this time. A second system which appears to offer interesting possibilities is that derived from the photolysis of organic azides, which is reported[32] to yield reactive species of the type [R-N:], nitrenes. The potential uses of species of this sort in forming bridged species by insertion in metal-metal bonds and in other instances has apparently not been investigated but at least appears to offer interesting possibilities. One may of course envision many other interesting systems and the foregoing list is meant to look at only a very few of these.

Conclusion

In conclusion, it appears reasonable to predict an increase in the application of photochemical conditions to the synthesis of compounds having limited thermal stability or reactivity which reaches useful proportions only at self destructive temperatures. The value of flash photolysis and low temperature irradiation in the study of reactive intermediates may also be expected to increase as more elaborate theoretical treatments and detection equipment are developed.

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THE JAHN-TELLER THEOREM

Woodrow Gordon McDugle, Jr. April 21, 1966

Introduction

H. A. Jahn and E. Teller postulated their renown theorem in 1937, but it was used very little until the early 1950's. In the last fifteen years or so, Jahn-Teller effects have been invoked many times to explain certain "anomalous" results in molecular structure studies. While many of these anomalies can be explained using this theorem, there are cases in which Jahn-Teller effects cannot be found where they should be present. But perhaps the greatest problem is in the mathematical formulation of Jahn-Teller effects. In this seminar I hope to convey some feeling for the Jahn-Teller Theorem and demonstrate some of the forms Jahn-Teller effects can assume.

The Jahn-Teller Theorem[1]

Using group-theoretical procedures, Jahn and Teller have pointed out that symmetrical structures in non-linear molecules are unstable with respect to certain nuclear vibrations provided that the electronic state is orbitally degenerate. If such a case exists, a molecule can lower its energy with a distortion of the nuclear configuration to one of lower symmetry with a resulting removal of the orbital degeneracy in first order.

Proof of the Jahn-Teller Theorem

Jahn and Teller proved their theorem by considering a nuclear configuration P which can be obtained from the symmetrical configuration P_o by the addition of a linear combination of a set of displaced configurations P_r. The Hamiltonian H for the electronic motion in the field of the nuclei, which are fixed in the configuration P, was expanded in a Taylor series about the symmetrical configuration as

$$H = H_o + \sum_j Q_j V_j + 1/2 \sum_{j,k} Q_j Q_k V_j V_k + \cdots \qquad (1)$$

where $V_j = (\partial H_o / \partial Q_j)$. Here Q_j is a function of the nuclear displacement coordinates and V_j is a function only of the electronic coordinates. Since the Hamiltonian must be invariant under all symmetry operations, Q_j and V_j must transform alike.

By using first order perturbation theory they were able to show that the Jahn-Teller "active" vibrations towards which a degenerate electronic state is unstable are those which give non-vanishing matrix elements of the form $\sum Q_j \langle \Psi | V_j | \Psi \rangle$. Here Ψ represents the wavefunction of the degenerate electronic state and spans the irreducible representation Γ in the point group of the molecule. Thus it becomes clear that in order for the initial degeneracy to be retained, that is for P_o to be stable, all of the matrix elements must vanish.

A molecule of O_h symmetry has the normal vibrational modes a_{1g}, e_g, $2t_{1u}$, t_{2g}, and t_{2u}. It can be shown by using the above proof that every possible orbital degeneracy of an octahedral molecule will be split by one or

more of these normal vibrational modes excluding the totally symmetrical vibrational mode, which, due to its very nature, cannot destroy the symmetry of a molecule. For example, for an even number of electrons and for Γ^1 the irreducible representation of a doubly degenerate electronic state, $(E_g \times E_g)_{sym} = (E_u \times E_u)_{sym} = A_{1g} + E_g$. Thus the doubly degenerate vibrational mode e_g will distort a doubly degenerate electronic state.

In the case of linear molecules only the quadratic and higher terms in the perturbation Hamiltonian (1) can remove a ground state electronic degeneracy. Such effects are called Renner effects.[2]

In their original paper Jahn and Teller stated that the distortion forces expected when a degenerate ground state exists will be smaller when the degenerate electrons are non-bonding than when they are bonding or anti-bonding. In a following paper Jahn considered spin degeneracy but this was shown to be of secondary importance compared to orbital degeneracy.[3] Jahn[3] and Avvakumov[4] have both shown that removal of the orbital degeneracy of a transition-metal ion can reduce the energy by 100 to 10,000 cm^{-1}, whereas removal of spin degeneracy of an orbital singlet well separated from other states only reduces the energy by 0.1 to 10 cm^{-1}—much less than the zero-point energy of a typical vibration.

A notable exception to the Jahn-Teller Theorem is a Kramers doublet which can not be split by electrostatic Jahn-Teller effects.[1]

Since the original derivation by Jahn and Teller, Clinton and Rice (1959)[5] have reformulated the theorem on the basis of the Hellmann-Feynman Theorem, and recently Ruch and Schonhofer (1965)[6] have presented a new proof which takes into account spin-orbit and spin-spin interactions of the electrons from the very beginning of the proof.

Mathematical Formulation of Jahn-Teller Effects

Van Vleck has derived the potential energy operator for the Jahn-Teller effect in doubly degenerate electronic states for molecules of symmetry in the cubic groups.[7] Only interactions that are linear in the normal coordinates Q are included in the operator and of these only Q_2 and Q_3 are included as they correspond to the doubly degenerate vibrational modes of e_g symmetry. Potential energy operators expanded in a Taylor series in powers of Q_2 and Q_3 to third order have been added by Van Vleck[7] and Öpik and Pryce.[8] Thus

$$\underline{V} = A \begin{bmatrix} -Q_3 & -Q_2 \\ -Q_2 & Q_3 \end{bmatrix} + 1/2\, M\omega^2(Q_2^2 + Q_3^2) + A'Q_3(Q_3^2 - 3Q_2^2)$$

If the doubly degenerate electronic ground state is taken to consist of the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals, the electronic eigenstates of this postential are $[\cos\frac{\theta}{2}|d_{x^2-y^2}\rangle + \sin\frac{\theta}{2}|d_{z^2}\rangle]$ and $[\sin\frac{\theta}{2}|d_{x^2-y^2}\rangle - \cos\frac{\theta}{2}|d_{z^2}\rangle]$.[9] It can be seen that the Jahn-Teller operator has split the doubly degenerate electronic state into the two singlet states shown in Figure 1.

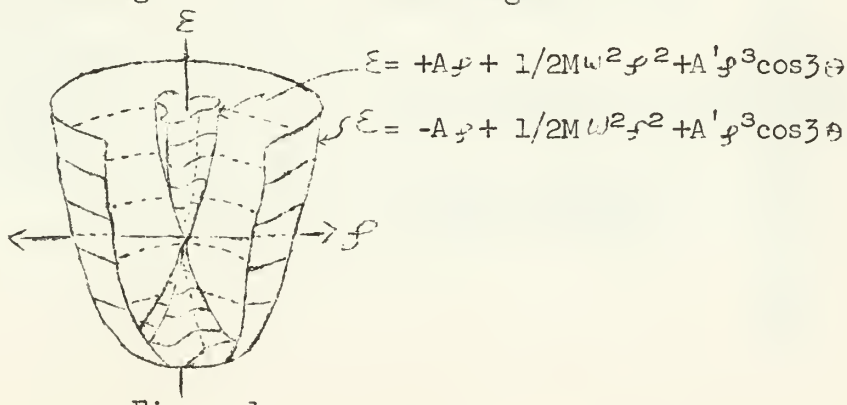


Figure 1

$A\rho$ is the Jahn-Teller energy term where A is a measure of the Jahn-Teller distortion forces and ρ corresponds to a distortion coordinate. A' indicates the size of the barriers against rotation from one distortion axis to another.

Several other mathematical and topological studies of Jahn-Teller effects have been presented and with an increasing degree of insight and sophistication.[9,10,11,12,13,14,15,16] However, many problems remain. An electrostatic model of Ballhausen and Liehr has been successful in predicting the distortion in VCl_4 relative to $TiCl_4$,[17,18] but the same model also predicts a compressed octahedron to be the most stable configuration for hexacoordinated Cu(II) complexes which is not correct.

Moffitt and Liehr have shown that if the coupling or interaction between an electronically degenerate state and some asymmetric nuclear displacement is sufficiently strong relative to the zero-point energy of the vibrational modes, the molecule or complex will undergo a static distortion to a new configuration of minimum energy.[19] Thus the ground state of the molecule will be confined to the lower potential sheet in Figure 1. However, if the coupling is less strong, or if the distortion forces tending to lower the symmetry of the electronically degenerate state are of the same order as the restoring forces encountered during typical vibrations, then, at best, the degenerate vibrational levels will be split and the electronic degeneracy will not be affected. In most cases this gives rise to a special coupling between the electronic and nuclear motions and the motion will not be confined to the lower electronic potential energy surface. This latter situation is known as the dynamical Jahn-Teller effect.

Infrared and Raman Effect Evidence of Jahn-Teller Effects

The hexafluorides (XF_6) of which there are presently 18 known,[20] perhaps exhibit the best documented cases of dynamic Jahn-Teller effects known. The hexafluorides are an excellent group to study for two reasons: (1) the high volatility of the hexafluorides makes it possible to study them in the gas phase where intermolecular forces are at a minimum, and (2) the study of an extensive series of homologous compounds makes possible a thorough test of the qualitative aspects of the Jahn-Teller Theorem.

Table I. Fifteen of the known hexafluorides and the lowest lying electronic state of the central atom based on an intermediate coupling scheme.[21]

X^{6+}		Lowest Lying Electronic State	Degeneracy	Comments	References
Mo	$4d^0$	A_{1g} ($J'=0$)	1		22
Tc	$4d^1$	Γ_8 ($J'=3/2$)	4		22,26
Ru	$4d^2$	T_{2g} ($J'=1$)	3		22,30
Rh	$4d^3$	Γ_8 ($J'=3/2$)	4	spin degeneracy only	22,30
W	$5d^0$	A_{1g} ($J'=0$)	1		21
Re	$5d^1$	Γ_8 ($J'=3/2$)	4		21,25
Os	$5d^2$	$E+T_2$ ($J'=2$)	5		21,26,27
Ir	$5d^3$	Γ_8 ($J'=3/2$)	4	spin degeneracy only	21,28,29
Pt	$5d^4$	A_{1g} ($J'=0$)	1		21
U	$5f^0$	A_{1g}	1		22
Np	$5f^1$	Γ_7	2	Kramers doublet	23
Pu	$5f^2$	A_{1g}	1		24
S	(Ne)	A_{1g}	1		22
Se	(Ar)$3d^{10}$	A_{1g}	1		22
Te	(Kr)$4d^{10}$	A_{1g}	1		22

As can be readily seen from Table I, TcF_6, RuF_6, ReF_6, and OsF_6 possess orbitally degenerate ground states and therefore are expected to exhibit Jahn-Teller distortions. Several meticulous analyses over the past few years have conclusively shown that these four Jahn-Teller candidates do undergo Jahn-Teller distortions, and these distortions are dynamic in character so that their octahedral structure is retained. The Raman active $\nu_2(e_g)$ vibration is a Jahn-Teller "active" vibration for octahedral molecules in degenerate ground states, and it has been found in Raman effect studies that the ν_2 band is barely discernable in three of the Jahn-Teller molecules (RuF_6 is photochemically unstable). In addition, the infrared active binary sum bands containing ν_2 are distorted compared to those of the normal hexafluorides.

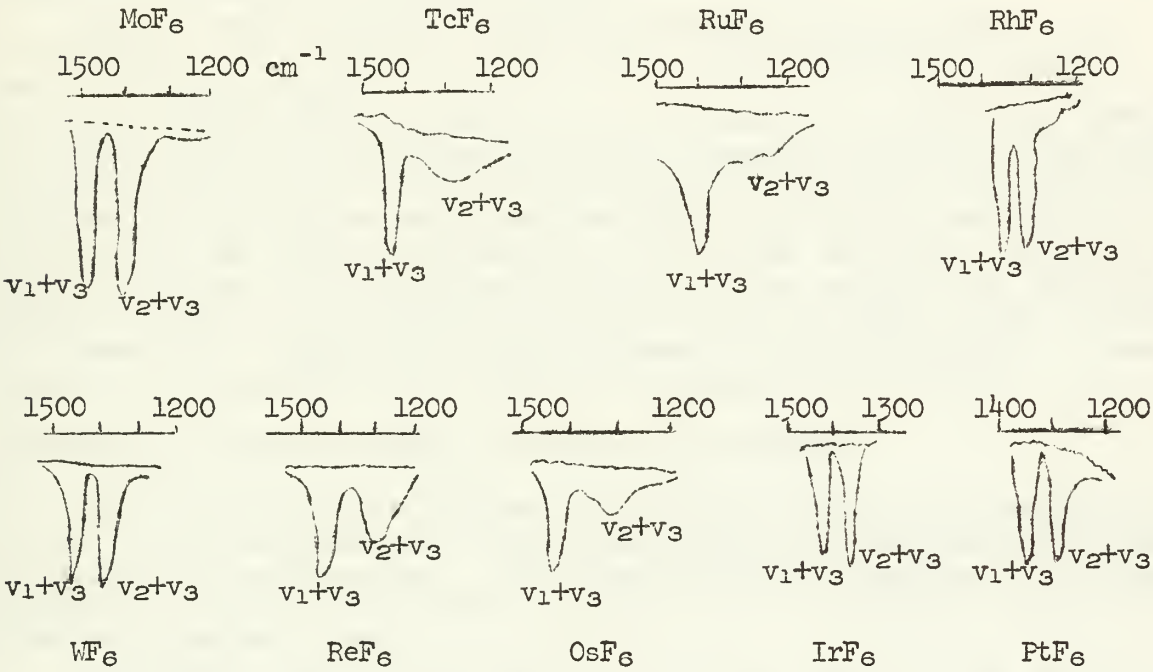


Figure 2. Band profiles for the ($\nu_1 + \nu_3$) and ($\nu_2 + \nu_3$) infrared active binary sum bands of the 4d and 5d transition metal hexafluorides.

Other infrared studies have indicated that a Jahn-Teller distortion occurs in manganic trisacetylacetonate relative to the ferric and chromic trisacetylacetonates as one of the fundamentals (e) of the manganic complex is split.[31]

Jahn-Teller effects have been reported in the Raman effect of $ReCl_6^{2-}$ and $OsCl_6^{2-}$ but they are not conclusive.[32]

Electron Spin Resonance Evidence of Jahn-Teller Effects

Electron spin resonance studies (ESR) of transition metal ions placed in highly symmetrical crystal structures have uncovered several interesting facets of the Jahn-Teller effect. Bleaney and Ingram (1950) first noticed that the high temperature ESR absorption of $CuSiF_6 \cdot 6H_2O$ diluted with $ZnSiF_6 \cdot 6H_2O$ is isotropic and that the low temperature absorption is anisotropic.[33] This

phenomena was explained earlier by Abragam and Pryce[34] and more recently by Liehr and Ballhausen[18] and M. C. M. O'Brien.[9] The magnetically dilute $CuSiF_6 \cdot 6H_2O$ in which the divalent copper is octahedrally surrounded has a g tensor value of 2.24 at room temperature, but at low temperature the ESR absorption is anisotropic giving a $g_\perp$ of 2.12 and $g_\parallel$ of 2.48. Evidently, at room temperature the Jahn-Teller distortion forces are weaker than the ordinary vibrational forces and the molecule is in a "time-averaged" octahedral configuration. Due to the $\cos 3\theta$ term in Figure 1, there are three possible equivalent tetragonal distortions separated by the three maxima. But at room temperature the molecule either passes over these barriers or resonates through them in a fashion somewhat similar to that in NH_3. At low temperature when the Jahn-Teller distortion forces become greater than the ordinary vibrational forces, the nuclear coordinates cease to follow the electronic motions exactly, and a transition from the previous dynamic case to the static case with a locked in tetragonal distortion occurs.

Similar results have been obtained for magnetically dilute $Cu_3La_2(NO_3)_{12} \cdot 24D_2O$,[35] Y^{2+} in CaF_2,[36] Pt^{1+}, Cu^{2+}, and Ni^{3+} in Al_2O_3,[37] and for La^{2+} in CaF_2.[38]

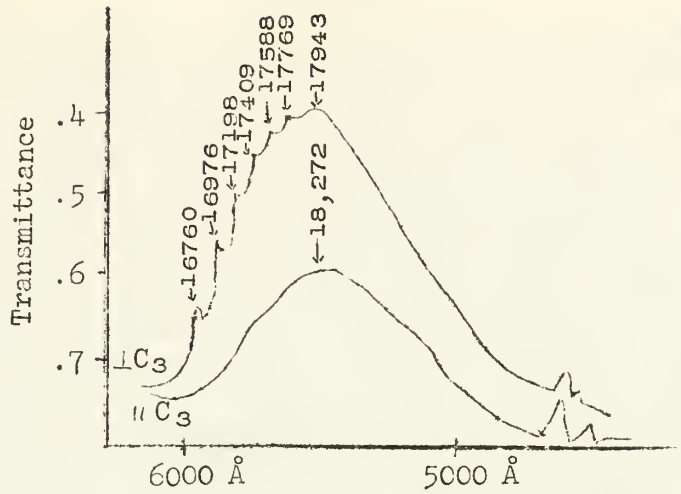
Other ESR absorption studies have been done on Ni^{1+} ($3d^9$) and Cu^{2+}($3d^9$) in single crystals of CaO[39] and in single crystals of MgO.[35,40] The ESR of these two ions in CaO is what one would expect as they have a high temperature isotropic ESR absorption and a low temperature anisotropic absorption. However, in the MgO lattice no evidence of distortion was found. Hatfield and Piper have shown that if lattice forces are strong enough, then Jahn-Teller distortions will be ineffective.[41] This explains the ESR results concerning Ni^{1+} and Cu^{2+} in MgO as MgO (Mg-O distance of 2.10 Å) is known to exert a stronger crystal field than CaO (Ca-O distance of 2.40 Å).[42]

Electronic Absorption Evidence of Jahn-Teller Effects.

Electronic absorption studies of Jahn-Teller molecules show Jahn-Teller effects in excited electronic states and these effects may be broken down into two general classifications: (1) the splitting or broadening of electronic spectral bands, and (2) uniquantal progressions of asymmetric vibrations on electronic spectral bands.

The classic case of splitting of electronic spectral bands is that of $Ti(H_2O)_6^{3+}$.[43] The one d electron is excited from the lower t_{2g} set to the antibonding e_g set where it experiences a Jahn-Teller distortion. Instead of seeing one band, one sees a band that is split almost into two bands. Other studies have been done on the cleaved absorption bands of the high spin systems $Fe(H_2O)_6^{2+}$ and K_2NaCoF_6[44] and on the asymmetric visible absorption bands of octahedral Cr(II) complexes.[18] Holmes and McClure have discussed the broadening in the d-d spectra of Jahn-Teller transition metal ions.[45] Sturge has done an interesting study on the Jahn-Teller effect in the $^4T_{2g}$ excited state of V(II) in MgO.[46]

There have been only a few abstracted cases of progressions in single quanta of asymmetric vibrations which have been discussed in terms of a Jahn-Teller effect.[47,48,49,50] Ford and Hill[47] and McClure[48] have studied the absorption spectrum in polarized light of Cr(III) in Al_2O_3 at low temperatures in the 5500 Å region. The $^4T_{2g} \leftarrow {}^4A_{2g}$ transition of octahedrally coordinated Cr(III) is broken down into a $^4E_{(1)} \longleftarrow {}^4A_{(0)}$ transition (polarized $\perp$ to C_3) and a $^4A_{(1)} \longleftarrow {}^4A_{(0)}$ transition (polarized $\parallel$ to C_3) in the C_3 symmetry site which Cr(III) occupies in Al_2O_3. The $^4E_{(1)} \leftarrow {}^4A_{(0)}$ transition is found to consist of a progression in single quanta of an asymmetric vibration on the long wavelength side of the band as shown in Figure 3. The progression consists



of several peaks (spaced in intervals of about 180 and 200 cm^{-1}) which have been assigned to the e vibrational mode of 194 cm^{-1} of the Al_2O_3 lattice. A uniquantal progression of an asymmetric vibration is not expected to appear in an allowed transition and should only occur if the excited state ($^4E_{(1)}$ in this case) is distorted so that the asymmetric vibration becomes totally symmetric under the lower symmetry of the distorted structure.[19] By the Jahn-Teller Theorem, an E electronic state in C_3 symmetry can couple with an e vibrational mode to give a non-vanishing matrix element of the form $\langle \Psi(^4E_{(1)}) | V_e | \Psi(^4E_{(1)}) \rangle$ and lower the symmetry. Here V_e is an appropriate operator for the vibrational perturbation of symmetry e. The appearance of such a progression is evidence that the excited state is a victim of Jahn-Teller distortion forces so as to destroy the C_3 symmetry and allow the asymmetric vibration to couple in. Further proof for a vibronic distortion is given in the fact that the $^4A_{(1)} \leftarrow {}^4A_{(0)}$ transition contains no vibrational fine structure.

Dunn has also discussed the effects of Jahn-Teller distortions on the visible and ultra-violet spectra of complex compounds.[51]

Structural Evidence of Jahn-Teller Effects

There exists good evidence for static Jahn-Teller distortions in the transition metal difluorides (MF_2) of rutile structure,[52] in the MF_3 series of VF_3 structure,[53] in the KMF_3 systems of a cubic perovskite structure,[54] and the fluorospinels K_2MF_4.[55] There also exists evidence for static distortions due to Jahn-Teller effects in systems other than the fluorides.[56,57]

Gyorgy and Schnettler have attributed the magnetic anisotropy induced in Ni and Mn ferrite at room temperature to preferentially oriented Jahn-Teller distortions.[58] Tanaka et al. have studied the effect of cooperative Jahn-Teller distortions on the Mössbauer absorption spectra in copper ferrite.[59]

Thermodynamic evidence of Jahn-Teller effects is scarce, but McClure[60] and Rossotti[61] have discussed some of its implications.

In Search of a Jahn-Teller Effect

In many cases Jahn-Teller effects are not as easy to substantiate as might seem from the previous evidence. For instance, Palmer and Piper have studied the optical spectra of tris(2,2'-bipyridine) copper(II) nitrate and found that the complex retains its D_3 symmetry and doubly degenerate ground state in solution and in the solid.[62] This is contrary to most Cu(II) complexes which

undergo some degree of Jahn-Teller distortion at room temperature. They credit this retention of trigonal symmetry to the rigidity of the bidentate ligands which confer immunity to Jahn-Teller distortion. If the complex does experience a Jahn-Teller effect at room temperature, it is dynamical. In keeping with this, Inskeep has found a splitting of certain bands in the infrared of the copper complex but not in the analogs of Co(II), Ni(II), and Zn(II).[63]

Another case at hand is that of Co(II) and Fe(II) in MgO for which studies have been unable to detect any distortions of the cubic symmetry.[64] Co(II) in an octahedral environment has a $^4T_{1g}$ ground state and Fe(II) has a $^5T_{2g}$ ground state. The basic reason for this lack of distortion in Co(II) and Fe(II) is that spin-orbit coupling is important in T states. Spin-orbit coupling removes the orbital degeneracy and leaves a Kramers doublet in Co(II) with $J = 1/2$. In Fe(II) spin-orbit coupling has reduced the orbital degeneracy to nearly a pure spin triplet. Ham has recently discussed the spin-orbit quenching of Jahn-Teller effects in some detail,[65] and Ballhausen has shown for square planar complexes that in the limit of large spin-orbit coupling, the Jahn-Teller coupling is completely quenched.[2]

What may appear at first to be a Jahn-Teller distortion, may actually be a distortion due to ligand inequivalences, spin-orbit coupling, or crystal lattice interactions. Therefore, care must be taken in invoking a Jahn-Teller distortion.

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OPTICAL AND ELECTRON SPIN RESONANCE SPECTRA OF NON-CUBIC TRANSITION METAL COMPLEXES IN CRYSTALS

Joseph A. Stanko April 26, 1966

Introduction

The complexes to be discussed are in the main mono-substituted amine complexes of cobalt, chromium and ruthenium. The polarized spectra of the complexes oriented in crystals allows information on the intensity mechanism of the absorption bands to be obtained. It also provides a means of obtaining the band splitting due to the reduction of the cubic symmetry. The electron spin resonance of the paramagnetic members of the series provides a more detailed description of the electron distribution in the ground states of the ions and in these non-cubic complexes, data on the splitting of the octahedral t_{2g} orbitals, which is difficult to obtain otherwise.

The Crystals

For the optical spectra the hexafluorosilicate salts of the monoacidopentammine cations, $[M(NH_3)_5X]^{+2}$, proved useful since they formed a series of isomorphous salts with a variety of X ligands. The crystal structure of one member of the series $[Co(NH_3)_5Cl]SiF_6$ was solved by X-ray diffraction techniques.

For the ESR the chromium, d^3, and ruthenium, d^5, complexes were diluted in the analogous diamagnetic rhodium or iridium salts e.g. $[Rh(Cr)(NH_3)_5Cl]Cl_2$. The crystal structures of these are known.[1]

Intensity Mechanism

For electric dipole transitions between the predominantly even d orbitals the source of the intensity could be either static, due to the equilibrium configuration of the nuclei lacking an inversion center, or vibronic and due to the motion of the nuclear framework. For trigonal complexes selection rules based on the equilibrium geometry of the complexes are fairly well obeyed and the intensity source identified as predominantly static.[2,3,4] In the tetragonal complexes studied here the band polarizations and temperature dependence reveal that we have examples of a case where the vibronically induced components are as large as, and of opposite polarization to components allowed in the fixed nuclei approximation.

The appearance of vibrational fine structure in some of the components and not in others is interpretable on the basis of the normal modes,[5] the orbitals involved in the transition and the Jahn Teller effect in excited electronic states.

Where the X ligand is fluoride, chloride or bromide, the intensity distribution for the various polarization is similar. However, with cyanide some differences are evident. A calculation of the intensity was performed in an effort to discover if this was a result of a change in the bonding situation for cyanide versus halide.

In contrast to the "d-d" transitions, the strongly allowed charge transfer transitions as observed in the halo-pentammines of ruthenium agree well with the selection rules for C_{4v} symmetry.

Energy Levels

The early application of crystal field theory and molecular orbital theory to the substituted ammine complexes was given by Yamatera.[6] Recently Wentworth and Piper[7,8] have reformulated the theory and have given the energy levels in terms of the differences in sigma and π antibonding powers of the X ligand versus the ammonia ligand. There have also been recent papers by other authors on the same subject.[9,10] All authors are in substantial agreement in the prediction that the π antibonding differences should reinforce the sigma antibonding differences in splitting of the first band and that they would tend to cancel each other in the second band.

The single crystal spectra reveal splittings in the second band which are smaller than theoretically predicted on the basis of sigma antibonding differences only, but agree with the predicted ordering of the band components. An exception is the fluoride complex where the individual components are clearly seen in the second band.

ESR

1) $Ru(NH_3)_5X^{+2}$; X = Cl, Br, I

Ruthenium(III) has a spin paired d^5 electronic configuration. The $^2T_{2g}$ ground doublet is split in a tetragonal field to a $^2B_2$ and an ^2E state. Including spin-orbit coupling, the ground state becomes a Γ_7. The g values for the complexes, their short spin-lattice relaxation times (spectra are only obtainable at liquid He temperature) along with their optical spectra confirm the ground state to be mainly $^2E(\Gamma_7)$. The one electron t_{2g} orbitals must thus have the ordering xz,yz > xy. The relative values of the g factors for the complexes disclose the relative splitting of the t_{2g} set and indicate the π antibonding power to be I < Br < Cl.

Hyperfine splitting of the electron spin resonance signal by the halide ligand was clearly resolved in the case of the iodide complex but must be less than the line width in the case of the chloride. In both instances the hyperfine appeared to be isotropic. This precluded obtaining any estimate of the amount of halide p-π orbital in the molecular orbital occupied by the unpaired electron.

2) $Cr(NH_3)_5X^{+2}$; X = F, Cl, Br

The interplay of spin-orbit coupling and the axial crystal field produces a zero field splitting of the spin levels and a three line spectrum is observed. The theory for the splitting has recently been given by McGarvey.[11] The angular variation of the spectrum is a strong function of the rhombic character of the site occupied by the paramagnetic complex. No ligand hyperfine was observed.

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INORGANIC REACTIONS AT HIGH TEMPERATURES

Robert L. Diebner May 3, 1966

Introduction

It is the purpose of this seminar to enumerate a few of the general characteristics of high temperature chemistry, to present thermodynamic reasoning to account for these characteristics, and to illustrate these points by examination of some high temperature inorganic systems, showing how useful information can be derived from such studies. The terminology "high temperatures" will pertain here to temperatures in the range 1,000°-3,000°K, and reactions will be confined to condensed phase-gas phase equilibria and gas phase-gas phase equilibria.

General Characteristics

When a gaseous system in contact with a condensed phase is heated, the partial pressures of the various species will not remain constant. The pressures will increase fast enough to offset any simplifying effect of increase in temperature that might be expected in a system at constant pressure. Thus high temperature gaseous systems with condensed phases will become more complex the higher the temperature.[1]

There are three principal ways in which high temperature systems become more complex:

1) Unfamiliar oxidation states and compounds with unusual formulas often occur at high temperatures. At these temperatures such common oxidation states as +1 for the alkali metals, +2 for the alkaline-earth metals, etc., are many times not the states found.

2) Gaseous molecules themselves become very complex. Molecules with 5, 10, or more atoms per molecule can be found.

3) In contrast to low temperature systems, which contain one or two principal species, one may have many different species of approximately comparable importance at high temperatures.

While there is no general principle at present which will account for the formation of the many less-common oxidation state species, the second and third characteristics listed above can be explained by simple thermodynamics. Let us consider the sublimation of some solid species $A_{(s)}$ to the gaseous monomer $A_{(g)}$ or alternately to $A_{2(g)}$ under equilibrium conditions as shown below:

$$A_{(s)} = A_{(g)} \qquad \Delta H_1^{\circ}$$
$$2A_{(s)} = A_{2(g)} \qquad \Delta H_2^{\circ}$$
$$A_{2(g)} = 2A_{(g)} \qquad \Delta H_d^{\circ}$$
$$2\Delta H_1^{\circ} = \Delta H_2^{\circ} + \Delta H_d^{\circ}$$

Since ΔS° of the first two reactions should be similar, the order of ΔF° for each of these two reactions should be approximately the same as the order of ΔH°. For many systems ΔH_d° is small compared to ΔH_1°, in which case ΔH_2° is much larger than ΔH_1°. In this instance, the monomer will have a higher partial pressure than the dimer at room temperature, but for the same reason, the dimer

partial pressure has a much higher temperature coefficient and so must increase with temperature the more rapidly of the two, so that the higher the temperature of the saturated vapor, the more comparable dimer and monomer concentrations become. Though ΔH_d^o is not always small compared to ΔH_1^o, the usual case is that $\Delta H_1^o < \Delta H_2^o$ and generally $P_{dimer}/P_{monomer}$ increases with temperature.[2] This example can be generalized[3,4] to trimers, disproportionation reactions and any sort of vaporization reaction. In general, the species which predominates at low temperatures will generally have the lowest heat of vaporization and all the other species, which are relatively unimportant at low temperatures, will have higher heats of vaporization. Therefore, the higher the temperature the more complex the vapor becomes with respect to the number of different species of comparable importance.[1]

Methods

All of the systems discussed here were analyzed using the mass spectrometer (magnetic sector type), probably the most sensitive and widely used instrument for high temperature systems. Construction and operational details have been given by Inghram and Drowart.[5] All of the studies presented were done using Knudsen effusion cells for sample holders. A Knudsen cell possesses a small orifice and a large sample area, so that thermal equilibrium is maintained within the cell.

One of the main purposes of these mass-spectrometric studies is the determination of $\Delta H^o_{reaction}$. This value is usually determined in two principal ways. The most direct approach is by use of the Clausius-Clapeyron equation (second law treatment):

$$\frac{d \ln K_{eq}}{d(1/T)} = -\frac{\Delta H_T^o}{R} \qquad (1)$$

By plotting $-\ln K_{eq}$ vs. $1/T$, the ΔH_T^o value is obtained from the slope of the plot. The other method (third law treatment) involves the use of the free-energy function, $-\left(\frac{F_T^o - H_o^o}{T}\right)$. This quantity can be calculated from statistical mechanics.[4,6] Free-energy functions have been tabulated for a great number of species.[7,8] Pressure determinations are made using standard relation[5,9] $P = kI^+T$, where k = constant for system studied, I^+ is the ion current, and T the temperature.

Alkaline-Earth Monofluorides

A mass spectrometric study of the vaporization of MF_2 + Al, where M = Mg, Sr, and Ba, has been carried out by Ehlert and workers.[10]

MgF_2 + Al

The important ion species found were: Mg^+, Al^+, MgF^+, AlF^+, and AlF_2^+ corresponding respectively to the parents $Mg_{(g)}$, $Al_{(g)}$, $MgF_{(g)}$ and $MgF_{2(g)}$, $AlF_{(g)}$, and $AlF_{3(g)}$. As in MgF_2 sublimation studies,[11] small amounts of MgF_2^+, $Mg_2F_3^+$ and $Mg_3F_5^+$ were observed. The equilibrium constant for the homogeneous reaction

$$AlF_{3(g)} + 2Mg_{(g)} = AlF_{(g)} + 2MgF_{(g)} \qquad (2)$$

was determined at several temperatures. Knowing the value of K_{eq} from pressure measurements, ΔF^{o}_{T} was calculated and combined with free-energy functions[8] to obtain $\Delta H^{o}_{298\ react} = 47.7 \pm 1.2$ kcal/mole. Using tabulated values for $\Delta H^{o}_{f\ 298}$ of $AlF_{3(g)}$, $AlF_{(g)}$, and $Mg_{(g)}$ of -286.7 ± 1.2,[8] -62.2 ± 0.5,[12] and 35.28 ± 0.01 kcal/mole respectively, and the dissociation energy of fluorine, 37 ± 0.3 kcal/mole,[8] the $D^{o}_{298}(MgF_{(g)})$ was found to be 107.3 ± 1.6 kcal/mole (4.67 ± 0.07 e.v.). A similar third law treatment of the heterogeneous reaction

$$2MgF_{(g)} = Mg_{(g)} + MgF_{2(s)} \qquad (3)$$

yielded a value of $D^{o}_{298}\ (MgF_{(g)}) = 105.5 \pm 1.2$ kcal/mole (4.59 ± 0.05 e.v.), in good agreement with the above value.

SrF_2 + Al and BaF_2 + Al Systems

Important species of each of these systems were found to be $Al_{(g)}$, $M'F_{(g)}$, $M'_{(g)}$, $AlF_{(g)}$, and $M'F_{2(g)}$, where M' = Sr and Ba. Values for D^{o}_{298} (M'F) for SrF and BaF were calculated in a manner similar to that given for MgF, giving $D^{o}_{298}(SrF) = 5.43$ e.v. and $D^{o}_{298}(BaF) = 5.83 \pm 0.1$ e.v.

A comparison of D^{o}_{298} (MF) values by various methods are given in Table I (tabulated in e.v.).

Table I

	MgF	CaF[13]	SrF	BaF
Equilibrium[10]	4.62 ± 0.1	5.44 ± 0.10	5.43 ± 0.1	5.83 ± 0.1
Electron Bombardment[10]	$\geq 4.8 \pm 0.6$	$\geq 4.9 \pm 0.9$	$\geq 5.1 \pm 0.9$	$\geq 5.7 \pm 0.9$
Ionic Model[14]	4.31	5.24	5.46	5.84
Spectroscopic[15]	3.2 ± 0.7	≤ 3.2	2.7 ± 1.0	3.0 ± 1.0

These equilibrium results correlate well with those calculated for an ionic model. For Mg, Ca, Sr, and Ba, the D(MF) values vary roughly as $[IP(M)]^{-1}$, but D(FM-F) is essentially constant. It should be noted that work of other groups[16,17] on BeF indicates a value for D(BeF) of about 6.3 e.v., substantially higher than the others.

Al_2O_3 System

Vaporization studies of the Al_2O_3 system using Mo and W cells have been carried out by Drowart, Inghram and workers.[18] Ionization efficiency curves show that at low electron energies the parents of observed ions O^+, Al^+, AlO^+, Al_2O^+ and $Al_2O_2^+$ are respectively, $O_{(g)}$, $Al_{(g)}$, $AlO_{(g)}$, $Al_2O_{(g)}$ and $Al_2O_{2(g)}$. The Al pressures measured initially for the Mo-Al_2O_3 system were close to those calculated for neutral conditions, but some reduction became evident after some time at higher temperatures. Reduction was found to be less in the W-Al_2O_3 system, and pressures from the latter system compared well with those calculated under neutral conditions using available data.[19-21]

From experimental pressures used to calculate ΔF^{o}_{T} and free-energy functions estimated in this study, the following heats of reaction were measured:

Table II

HEATS OF REACTION ΔH_0^0 (KCAL/MOLE)

Reaction	Al_2O_3 + Mo	Al_2O_3 + W	AVE.
$Al_2O_{2(g)} \rightarrow 2AlO_{(g)}$	134.3	135.8	135.0 ± 5
$Al_2O_{(g)} \rightarrow AlO_{(g)} + Al_{(g)}$	131.0	131.7	131.4 ± 5
$AlO_{(g)} \rightarrow Al_{(g)} + O_{(g)}$	115.5	113.9	114.7 ± 5
$Al_2O \rightarrow 2Al_{(g)} + O_{(g)}$	245.3	243.4	244.4 ± 7

The atomization energy of $Al_2O_{(g)}$, $D_0^0 = 245 \pm$ kcal/mole or $D_{298}^0 = 247 \pm 7$ kcal/mole, agrees well with $\Delta H_{298}^0 = 247 \pm 7$ kcal/mole from thermochemical measurements[20] and $\Delta H_{298}^0 = 256 \pm 7$ kcal/mole, based on second law measurements of ΔH_f^0 ($Al_2O_{(g)}$) from Al-Al_2O_3 measurements.[22] A recent investigation[23] on vaporization of Al_2O_3 done by thermal imaging techniques has yielded values in agreement with these studies. In addition, an infrared spectrum of Al_2O trapped in argon and krypton matrices has been recently observed[24] from which the molecular symmetry of $Al_2O_{(g)}$ has been concluded to be C_{2v}.

Polymerization

Several mass-spectrometric studies have been made on the vaporization of some of the IVB oxides. Going from those of Si,[25] to those of Ge, Sn, and Pb, the number of polymers detected and their concentrations increase regularly.

Sn Oxides

Recent experiments made by Colin and workers[26] show that vaporization of $SnO_{2(s)}$ follows the reaction:

$$SnO_{2(s)} \longrightarrow \frac{1}{n}(SnO)_{n(g)} + \frac{1}{2}O_2 \qquad (n = 1,2) \qquad (4)$$

Vaporization of $SnO_{(s)}$, which is known to disproportionate to $Sn_{(l)}$ and $SnO_{2(s)}$ in this temperature range (1030°-1200°K),[27,28] is found to follow:

$$\frac{n}{2}[SnO_{2(s)} + Sn_{(l)}] \longrightarrow (SnO)_{n(g)} \qquad (n = 1 \text{ to } 4) \qquad (5)$$

From second law treatments, standard enthalpy changes were found for the reaction

$$(SnO)_{n(g)} \longrightarrow nSnO_{(g)} \qquad (n = 1 \text{ to } 4) \qquad (6)$$

and third law entropies found for dimer, trimer, and tetramer. The SnO-SnO bond strength tends toward the heat of sublimation of monomer, calculated from ΔH_f^0 $(SnO)_{(s)}$.[29] This fact suggests that the gaseous polymers may have structures and binding forces closely related to those of the lattice.

Ge Oxides

Second law treatments[30] for GeO vaporization yielded ΔH^{o}_{react} for:

$$(GeO)_{n\,(g)} \longrightarrow nGeO_{(g)} \qquad (n = 2,3) \qquad (7)$$

The latter were obtained for vaporization of $GeO_{(am)}$, $GeO_{2(gl)} + Ge_{(c)}$, and $GeO_{2(hex)} + Ge_{(c)}$. [$GeO_{(am)}$ disproportionates to $GeO_{2(hex)} + Ge_{(c)}$].

Pb Oxides

Enthalpy changes and entropies were similarly obtained for:[31]

$$(PbO)_{n\,(g)} \longrightarrow n(PbO)_{(g)} \qquad (n = 1 \text{ to } 4) \qquad (8)$$

$(PbO)_5$ and $(PbO)_6$ were also found, but in such low concentration that no second law values could be obtained for these species. The average PbO-PbO bond in $(PbO)_n$ and the energy required to abstract one PbO from a given polymer show the same trend, and this value is quite close to the heat of sublimation, as was the case for SnO and GeO. A comparison of MO-MO bond strength is given below for the dimerization reaction.

	MO-MO Bond
$(GeO)_{2(g)} \longrightarrow 2GeO_{(g)}$	44.7 ± 3 kcal/mole
$(SnO)_{2(g)} \longrightarrow 2SnO_{(g)}$	66.8 ± 4 kcal/mole
$(PbO)_{2(g)} \longrightarrow 2PbO_{(g)}$	63.4 ± 4 kcal/mole

Graphite Vaporization

The vapors of many of the elements are known to consist of polymers. A mass-spectrometric study of the vapor over graphite by Drowart, Inghram, and workers,[32] have shown that the vapor consists of C^+, C_2^+, C_3^+, C_4^+, and C_5^+ which correspond at low electron energies to the direct ionization of the corresponding neutral molecules. Very small concentration of C_6^+ and C_7^+ also were observed. From previous mass-spectrometric studies of graphite,[33] ΔH^{o}_{o} = 169.58 kcal/mole has been determined for the sublimation of atomic carbon and was taken here[32] as a standard for a second law treatment of vaporization enthalpies. The latter values and those computed from free-energy functions[34] are compared in Table III.

Table III - ΔH^{o}_{o} in kcal/mole

	$-(F^{o}-H^{o}_{o})/T$ (cal/mole·°K) 2000°K	2500°K	3000°K	2nd Law	3rd Law	AVE C-C Bond
C_2	56.39	58.27	59.82	195.8 ± 1.7	198.0 ± 1.7	141.2
C_3	61.82	64.59	66.93	186.7 ± 1.5	188.1 ± 2.3	160.4
C_4	74.95	78.75	81.98	229.5 ± 7.1	240.5 ± 5.8	146.0
	73.70	77.50	80.73	229.5 ± 7.1	237.5 ± 5.8	147.0
C_5	80.96	85.79	89.91	232.5 ± 5.3	240.3 ± 5.8	151.9
	78.46	83.29	87.41	232.5 ± 5.3	234.3 ± 5.8	153.4
C_6	90.34	96.20	101.21	- - - -	≥ 280	≤ 148
C_7	95.10	101.99	107.89	- - - -	≥ 270	≤ 152

The average C-C bond energy is seen to be larger for odd-numbered species than for even-numbered ones, as predicted by a molecular orbital approach by Pitzer and Clementi.[34,35]

Other Group IVB Elements

Polymeric species have also been observed for the other elements of Group IVB. In the vapor over silicon at 1660°K., evidence for $Si_{(g)}$ through $Si_{7(g)}$ was found.[36] From other work[37] the dissociation energies for the reactions

$$Si_{2(g)} \longrightarrow 2Si_{(g)} \qquad \Delta H_0^0 = 75 \pm 5 \text{ kcal/mole} \qquad (9)$$

$$Si_{3(g)} \longrightarrow Si_{2(g)}^{+}, Si_{(g)} \qquad \Delta H_0^0 = 100 \pm 5 \text{ kcal/mole} \qquad (10)$$

indicate an alternation in stabilities similar to that found for graphite.

Mass-spectrometric studies[38,39] for germanium vapor have reported polymers $Ge_{(g)}$ through $Ge_{7(g)}$ with the polymeric species accounting for about 20% of the vapor at 1370°K. Enthalpies[38] for the reactions

$$Ge_{2(g)} \longrightarrow 2Ge_{(g)} \qquad \Delta H_0^0 = 64 \pm 5 \text{ kcal/mole} \qquad (11)$$

$$Ge_{3(g)} \longrightarrow Ge_{2(g)} + Ge_{(g)} \qquad \Delta H_0^0 = 89 \pm 5 \text{ kcal/mole} \qquad (12)$$

again show the alternation trend observed for carbon and silicon.

Evidence for polymers $Sn_{(g)}$ through $Sn_{5(g)}$ has been found at 1200°K.[39], but the fraction of polymeric species is less than 1%. The evaporation of lead at 800°K has shown[39] no polymer higher than Pb_2 and even its concentration was very low.

Conclusion

The cases presented here are only a few examples of a rapidly expanding new field in chemistry. The future of high-temperature chemistry is almost beyond prediction when one considers that in the past 100 years organic chemists, working in a limited temperature range, have succeeded in making over a million compounds from only five or six elements, while present-day high temperature chemists have available more than 100 elements and a temperature range of 10^5°K.[40] There is little doubt that thousands of new chemical materials will be prepared within the next few years by high temperature techniques. These compounds will probably be largely endothermic molecules that have become important species at high temperature, are quenched to low temperature, and are then maintained in useful form because of slow reaction rates for their conversion to more thermodynamically stable systems. While preparation of these compounds may not be difficult, many new techniques will have to be developed to use these species successfully.

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ORGANOMETALLIC INSERTION REACTIONS

Wayne P. Anderson May 5, 1966

Introduction

Organometallic insertion reactions of the type shown in equation (1) have been studied extensively only in recent years.

$$A - B + Z \longrightarrow A - Z - B \qquad (1)$$

However, they have been proposed as intermediates in many reactions the products of which have an appearance quite unlike that of A-Z-B.[1,2,3,4] Because of the usefulness of the insertion or corresponding elimination products in the syntheses of novel organometallic compounds and the probability of their formation as intermediates in the syntheses of many organic compounds in the presence of organometallic catalysts,[2] it is of interest to study these reactions in greater detail.

The inserting group may be one of two kinds. The first yields a product in which Z is only one atom of a molecule, such as S in SO_2. The second produces a product in which two atoms of a molecule have been inserted, such as C-S in CS_2. In the latter case, the reaction can be equally well classified as an addition of the organometallic compound, A-B, across the double bond of an unsaturated group. The form of the reaction, however, is still that given by (1).

In this seminar the insertion and elimination of species of both types will be discussed. The mechanisms of the reactions and the structures of the resulting products will be examined.

Carbon Monoxide

The most thoroughly studied of the insertion and elimination reactions is that of carbon monoxide. First reported by Coffield and his associates,[5] the CO insertion has been the object of various studies with regard to the stereochemistry, mechanism, and structure.

A) Reactions

The reactions of $RMn(CO)_5$ and $RCo(CO)_4$ with various ligands have been reported:

$$CH_3Mn(CO)_5 + L \longrightarrow CH_3COMn(CO)_4L \qquad (2)$$

where L = CO,[5] PR_3,[6] AsR_3,[6] SbR_3,[6] $C_6H_{11}NH_2$,[9] I^-,[10], or $C_6H_{11}NHCH_3$.[21]

$$RCo(CO)_4 + L \longrightarrow RCOCo(CO)_3L \qquad (3)$$

where L = CO[7] or PR_3.[7]

$$PhMn(CO)_5 + L \longrightarrow PhMn(CO)_4L \qquad (4)$$

where L = PR_3,[6] AsR_3,[6] or SbR_3.[6]

Even in the presence of excess PPh_3, only the monosubstituted derivative is formed.[6,7] However, when L = $(RO)_3P$,[6,8] $(PhO)_2PCH_3$,[6] or $Ph_2PCH_2CH_2PPh_2$ [6] the disubstituted derivative can be prepared.

Some interesting variations on the above reactions have been found. If $CH_3Mn(CO)_5$ is allowed to react with PPh_3 in an open system at room temperature, cis-$CH_3Mn(CO)_4PPh_3$ is formed.[13] Furthermore, the reaction[6] of $PhMn(CO)_4PPh_3$ with CO at 20°, 200 atm. gives $PhCOMn(CO)_5$ for which the proposed mechanism is:

$$\begin{array}{ccccc} PhMn(CO)_4PPh_3 & \longrightarrow & PhCOMn(CO)_3PPh_3 & \longrightarrow & PhMn(CO)_4 + PPh_3 \\ & & & & \downarrow CO \\ & & PhCOMn(CO)_5 & \xleftarrow{CO} & PhMn(CO)_5 \end{array} \qquad (5)$$

Many of the fluorocarbon analogues of the above acyl compounds have been prepared by the reaction of the sodium salt of the metal carbonyl with perfluoro acid anhydrides[12] or perfluoroalkyl halides.[16] Although these compounds can be decarbonylated, they have not been formed by the direct reaction of the perfluoroalkyl compound with a ligand as described above.[11]

Although they have been studied less than the manganese and cobalt systems, the following compounds have also been prepared by carbon monoxide insertions:

$C_5H_5Mo(CO)_3COC_2H_5$ [15]

$(Ph_3P)_2RhCl_2COC_2H_5$ [17]

$MX(COR)[P(C_2H_5)_3]_2$ [18]

M = Pt or Pd
X = Cl, Br, I
R = Alkyl or aryl

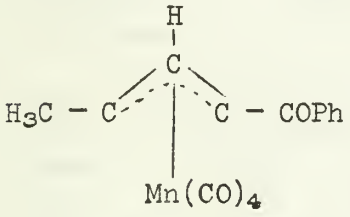
$CH_2 = CHCH_2CO\overset{\overset{CO}{|}}{\underset{\underset{CO}{|}}{Ni}}X$ [19]

$C_5H_5Fe(CO)L(COCH_3)$ [22]

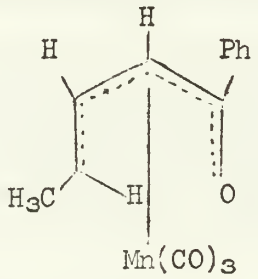
L = CO, PPh_3, $P(OPh)_3$, $P(C_4H_9)_3$, $P(CC_4H_9)_3$

In addition, many acyl compounds which have not been prepared by carbonylation reactions will decarbonylate[20] as do the cobalt and manganese acyl and perfluoroacyl derivatives.

An interesting compound has recently been prepared[23] by reacting phenylmanganese pentacarbonyl with butadiene. If (I) which is first formed is heated, (II) is obtained.



(I)



(II)

IR and NMR were used to identify the product.

B) Stereochemistry

In recent months considerable interest has developed over the stereochemistry of the acyl derivatives of methyl-manganese pentacarbonyl. Kraihanzel and Maples[13] found that in the reaction of the above with PPh_3 a product containing 70% trans isomer and 30% cis isomer of the acyl derivative was obtained. Calderazzo and Noack[10] also found a mixture of isomers to be present in the reaction with LiI to form $Li[RCOMn(CO)_4I]$.

Mawby, et al.[14] made use of stereochemistry in determining that methyl migration rather than carbonyl insertion occurs in reaction (6).

$$CH_3Mn(CO)_5 + PPh_3 \longrightarrow CH_3COMn(CO)_4PPh_3 \qquad (6)$$

Inasmuch as the cis isomer was formed in the decarbonylation of trans-$CH_3COMn(CO)_4PPh_3$, they concluded that the former mechanism is correct.

C) Rate Studies and Mechanism of Formation of Acyl Derivatives

Mawby, et al.[21] studied the reaction of methyl-manganese pentacarbonyl with various amines and phosphines. They found that in good donor solvents such as THF, nitromethane, bis(β-ethoxyethyl)ether, and bis(β-methoxyethyl)ether the rate of reaction with cyclohexylamine was independent of the amine concentration. However, in methanol, mesitylene, and n-hexane there was a dependence upon the concentration of the ligand. In the case of other ligands, the rate expression also was influenced by the solvent. Therefore, they proposed:

$$CH_3Mn(CO)_5 \xrightarrow{:S} CH_3COMn(CO)_4S \xrightarrow{L} CH_3COMn(CO)_4L + :S\,. \qquad (7)$$

This mechanism was also consistent with the data obtained by Calderazzo and Cotton[24] for the reaction of methyl-manganese pentacarbonyl with carbon monoxide which indicated that rate = $k[CO][CH_3Mn(CO)_5]$. Calderazzo and Cotton[25] later confirmed that the reaction with PPh_3 in diethoxydiethyl ether is independent of phosphine concentration.

Heck[26] found that the rate of reaction of PPh_3 with $RCOCo(CO)_4$ to give $RCOCo(CO)_3PPh_3$ is first order in $RCOCo(CO)_4$. He proposed (8).

$$RCOCo(CO)_4 \xrightarrow{slow} RCOCo(CO)_3 + CO \qquad (8)$$

$$RCOCo(CO)_3 + PPh_3 \longrightarrow \text{Product}$$

He studied the effect of electronic and steric factors on the rate and was able to relate his data to the above mechanism.

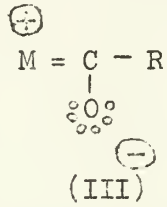
Recently Bibler and Wojcicki[22] investigated the reaction of $C_5H_5Fe(CO)_2CH_3$ with various phosphines and phosphites. They found that yields of better than 95% of π-$C_5H_5Fe(CO)L(COCH_3)$ were obtained in THF, 20-50% in diethyl ether, and none in n-hexane. They also found that when $(C_2H_5)_2S$, p-$CH_3C_6H_4NH_2$, p-$ClC_6H_4NH_2$, and I^- were used as ligands, no reaction occurred in THF. Thus, they proposed that the solvent-assisted mechanism is operative with the π-bonding ability of the ligand also being important.

D) Bonding and Stability of the Acyl Derivatives

Hieber, et al.[27] found that the tendency of perfluoroacyl manganese carbonyl derivatives, $R_fCOMn(CO)_4L$, to decarbonylate decreased with increasing basicity of L. They also found that increasing the length of the perfluoroalkyl chain caused a lowering of the decarbonylation temperature. However, the above derivatives are less likely to eliminate CO than are the compounds $R_fCOMn(CO)_5$.[28] Since in the decarbonylation of $RCOMn(CO)_5$ a coordinated CO rather than the acyl CO is lost,[16] King and Bisnette proposed[20] that the tendency to eliminate CO is inversely proportional to the strength of the metal-carbon monoxide bond.

Other facts which have been reported are that the perfluoroacyl derivatives are more stable than the acyl derivatives,[20] and the acyl cobalt tetracarbonyls are more stable than their alkyl analogues.[2] Also, many acyl iron compounds cannot be thermally decarbonylated,[16,20,30] although $RCOFe(CO)_2C_5H_5$ can be decarbonylated photolytically.[20]

Infra-red spectroscopy has been used frequently to obtain information concerning the bonding in the acyl compounds. The acyl carbonyl stretch occurs at a much lower frequency in these compounds than in aliphatic ketones.[29] This has been attributed to a contribution from resonance structure (III) which tends to increase the stability of these compounds.[30]



(III)

As R- or RCO- becomes more electronegative, the terminal CO frequency increases indicating increased backbonding to these groups.[12] Interestingly, perfluoroalkyl and analogous perfluoroacyl groups appear to have about the same electronegativity.[12,20]

Dipole moment measurements indicate[12] that if R is a saturated group (e.g. CH_3^-, $PhCH_2^-$) the bonding in the acyl manganese compounds is nearly independent of R.

Sulfur Dioxide

Insertion and elimination reactions involving sulfur dioxide have only recently been reported.[31,32] Although the data are somewhat limited, it is interesting to compare the results of these investigations with those found for carbon monoxide.

Bibler and Wojcicki[31] found that if an alkyl or aryl cyclopentadienyliron carbonyl were reacted with liquid sulfur dioxide, SO_2 insertion occurred:

$$\pi\text{-}C_5H_5Fe(CO)_2R + SO_2 \xrightarrow[-60^\circ]{-40^\circ \text{ to}} C_5H_5Fe(CO)_2SO_2R \qquad (9)$$

The yields were better than 90% for alkyl derivatives and about 35% for aryl derivatives. Similar insertions were found to occur with HgR_2,[33] $CH_3C_5H_5Mo(CO)_3$,[34] and $RMn(CO)_5$.[35]

The structure of these complexes has been elucidated through the use of IR and NMR.[31,35] The proposed bonding involves M-S-R attachment. Infrared spectra indicate[32,35] that an appreciable amount of backbonding from the metal to the sulfur occurs as in the case of the acyl compounds.[30]

No kinetic studies have as yet been made on these reactions. Therefore, either a mechanism involving an acyl-sulfur dioxide intermediate complex or one involving direct SO_2 attack on the metal is possible.[31] In any case it is believe that alkyl migration occurs as it does in the CO insertion reactions. It is significant, however, that no acyl intermediate has been isolated although a strong solvent-dependence has been found[36] as in the acyl formations.

The fact that no sulfur dioxide-acyl complex has been isolated may well be related to the fact that few sulfur dioxide complexes are known. Those which have been reported include:

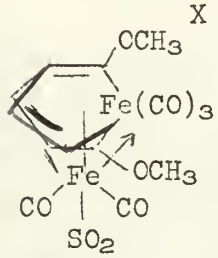
$[IrCl(CO)(PPh_3)_2SO_2]$ [37]

$[RhCl(CO)(PPh_3)_2SO_2]$ [37]

$[RuCl_2(PPh_3)_2SO_2]$ [37]

$C_6X_6Cr(CO)_2SO_2$ [38]

X = H, CH_3



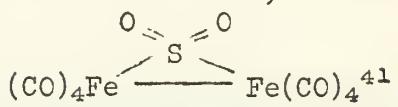
[41]

$C_5H_5Mn(CO)_2SO_2$ [39]

$[Ru(NH_3)_4XSO_2]X$ [40]

$[Ru(NH_3)_5SO_2]X_2$ [73]

X = Cl, Br



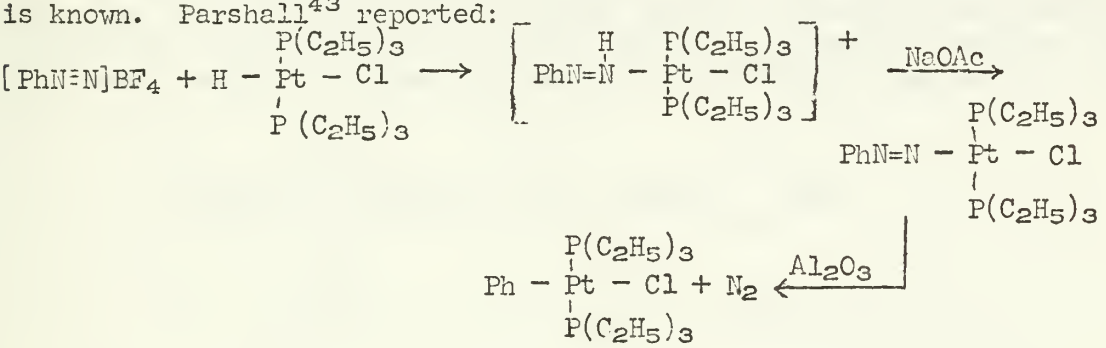
[41]

$[Ru(NH_3)_4(H_2O)SO_2](NO_3)_2$ [40]

Closely related to the above insertion reactions are the SO_2 elimination reactions reported by Collman and Roper[32] and Baucom.[42] They found that if $[IrClCO(PPh_3)_2]$ were reacted with RSO_2Cl a sulfonyl complex $[IrCl_2CO(PPh_3)_2SO_2R]$ could be prepared. When R = C_6H_5 or $CH_3C_6H_4$, heating the sulfinate caused elimination of sulfur dioxide to form $[IrCl_2CO(PPh_3)_2R]$. When R = alkyl, p-chlorophenyl, p-nitrophenyl, or p-methoxyphenyl no elimination was observed.

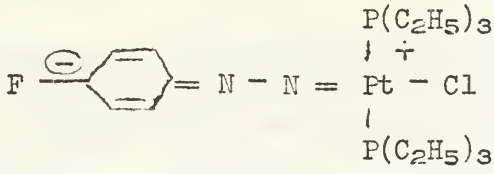
Nitrogen

Although there are no examples of nitrogen insertion reported, one nitrogen elimination reaction similar to the decarbonylation and SO_2 elimination reactions is known. Parshall[43] reported:



(10)

By studying the ^{19}F NMR of the p-fluorophenyl derivative[43,44] he determined that resonance structure (IV) plays an integral part in the bonding of the complex.



(IV)

Again back-bonding is important.

King and Bisnette[45] reacted $[p\text{-}CH_3OC_6H_4N{\equiv}N]BF_4$ with $NaMo(CO)_3C_5H_5$ and obtained $CH_3OC_6H_4N{=}N\text{-}Mo(CO)_2C_5H_5$. However, chromatography of this compound on an alumina column gave no N_2 elimination.

Carbenes

Dihalocarbene insertions into mercury-halogen bonds have been a disputed issue since their proposal by Reutov and Lovtsova[75,76] in order to explain (11).

$$PhHgX + CHX_3 \xrightarrow{t\text{-}BuOK} PhHgCX_3 + KX + t\text{-}BuOH \qquad (11)$$

Seyferth, et al.[77,78,79,80] have argued that their experimental evidence is better explained by a mechanism involving nucleophilic displacement of X in PhHgX by CX_3^-. A displacement process has also been favored by Logan.[81] For reactions in neutral solvents, however, both Lundgrebe and Mathis[82] and Seyferth, et al.,[83] have found that dihalocarbene insertion occurred.

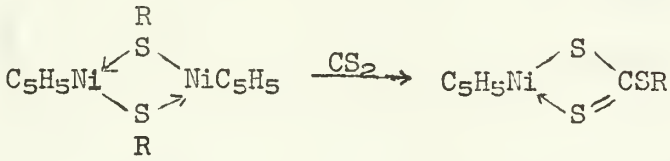
The use of $PhHgCCl_2X$ to insert dihalocarbenes into Si-H and Ge-H bonds has also been reported.[84] However, such an insertion did not occur with the Sn-H bond.[85] Carbene insertions possibly occur in the formation of many other $M\text{-}CH_2\text{-}X$ linkages.[86]

The only example of a carbene insertion into a transition metal-halogen bond was recently reported by Mango and Dvoretzky.[87] They found:

(12)

Carbon Disulfide

Carbon disulfide insertion reactions have been shown to be quite common. These are of a different type than the examples discussed previously in that a two-atom insertion occurs. Bladon, Bruce, and Knox[46] found that reaction (13) would explain the time dependence of the NMR spectrum of (V) in CS_2.



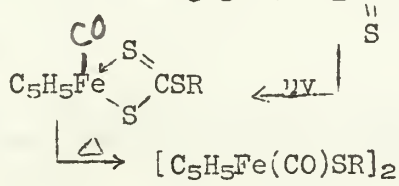
(V) (VI)

(13)

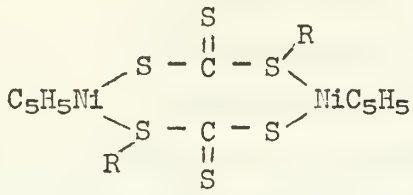
Similar results were obtained[47] with $C_5H_5Mo(CO)_3SR$ and $C_5H_5W(CO)_3SR$. However, either the iron analogue of (VI) or $[C_5H_5Fe(CO)SR]_2$ can be obtained from $C_5H_5Fe(CO)_2X$:

$$C_5H_5Fe(CO)_2X \longrightarrow C_5H_5Fe(CO)_2SR \xrightarrow{CS_2} [C_5H_5Fe(CO)SR]_2 \qquad (14)$$

$$C_5H_5Fe(CO)_2X \longrightarrow C_5H_5Fe(CO)_2SCSR \qquad (15)$$



Knox[47] has suggested two possible mechanisms for the nickel reaction. The first involves intermediate (VII), while the second consists of nucleophilic substitution of CS_2 into dissociated $[C_5H_5NiSR]_2$.



(VII)

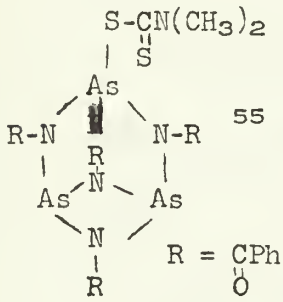
Breederveld[48] reported the reversible insertion of CS_2 into $(CH_3)_3SiN(C_2H_5)_2$ to form $(CH_3)_3Si\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}N(C_2H_5)_2$. This reaction requires the presence of free diethylamine to occur.[49] However, in the reaction of $(CH_3)_3SnN(CH_3)_2$ with CS_2[50] no free amine is necessary suggesting that a different mechanism is operative. A four-center mechanism was proposed[50] for the last reaction.

Carbon disulfide insertions have also been postulated to account for the formation of the following compounds:[74]

$R_3SnS\text{-}\underset{\underset{S}{\|}}{C}\text{-}OCH_3$ [51]

$RZn\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}NR'_2$ [52]

$R_3Ge\text{-}S\text{-}\underset{\underset{S}{\|}}{C}\text{-}N(CH_3)_2$ [53]

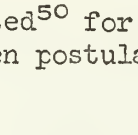


R = CPh

$M(\underset{\underset{S}{\|}}{S}CNR_2)_X$ [61]

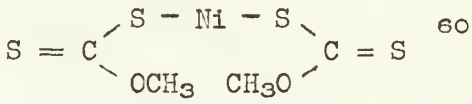
M = Ti, Zr, Hf, V, Nb, Ta

$As(S\text{-}\underset{\underset{S}{\|}}{C}NR_2)_3$ [54,56]



R = C_4H_9, C_2H_5

M = Na,[57] K,[58], Cu[59]



[60]

$R\text{-}\underset{\underset{S}{\|}}{C}\text{-}SM$

R = alkyl or aryl

M = Li,[62] Na,[62,63]

Carbon disulfide insertions have been proposed[64] to explain the catalytic effect of certain CS_2-organometallic systems on the polymerization of methyl methacrylate.

Metal-Metal Bond Insertions

Two types of insertions have been found to occur between metal-metal bonds. The first consists of addition across the double bond of an olefin or the triple bond of acetylenic species. The following examples demonstrate the scope of these reactions:

$$A\text{-}B + F_2C = CF_2 \longrightarrow A(F_2CCF_2)_nB \quad n \geq 1 \tag{16}$$

$A\text{-}B = (CH_3)_3SnMn(CO)_5$ [65,66]

$(CH_3)_3GeMn(CO)_5$ [66]

$(CH_3)_3SnSn(CH_3)_3$ [65,67]

$(CH_3)_2AsAs(CH_3)_2$ [68]

$$X\text{-}Y + F_3CC{\equiv}CCF_3 \longrightarrow X(F_3CC{=}CCF_3)Y \tag{17}$$

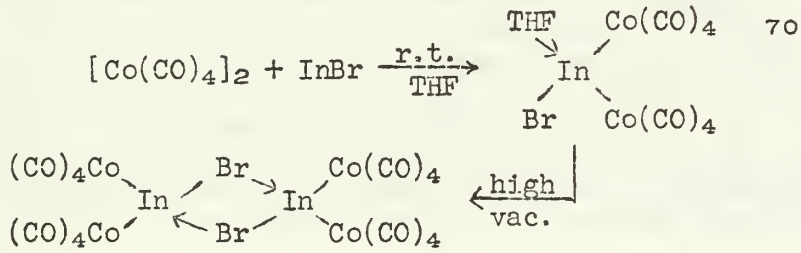
$X\text{-}Y = (CF_3)_2AsAs(CF_3)_2$ [69]

$(CH_3)_2AsAs(CH_3)_2$ [68]

Clark, et al.[65] have proposed a free-radical mechanism for the photolytic reaction of hexamethylditin with tetrafluoroethylene. Clark,[66] however, believes an ionic or four-center mechanism must be involked to explain the Sn-Mn and Ge-Mn reactions.

Some interesting observations have been made on the above reactions. First, no insertion occurs[66] with ethylene and $(CH_3)_3SnMn(CO)_5$ or $(CH_3)_3GeMn(CO)_5$. Similarly, no insertion product is obtained[69] with $CF_3C{\equiv}CCF_3$ and $(CH_3)_3SiSi(CH_3)_3$ or $(C_2H_5)_3Ge\text{-}Ge(C_2H_5)_3$, probably because of the greater strength of the Ge-Ge and Si-Si bonds than the Sn-Sn bond. In the photolytic reaction of $(CF_3)_2As\text{-}As(CF_3)_2$ with $CF_3C{\equiv}CCF_3$, only the trans isomer was formed[69] whereas a mixture of isomers was obtained[68] in the thermal reaction of $(CH_3)_2As\text{-}As(CH_3)_2$ with hexafluoro-2-butyne.

The second type of metal-metal bond insertion yields a product with a metal-metal-metal bond. Those reported include:



(18)

$$[C_5H_5Fe(CO)_2]_2 + GeI_2 \xrightarrow[C_6H_6]{\text{reflux}} [C_5H_5Fe(CO)_2]_2GeI_2 \quad [71] \tag{19}$$

$$[C_5H_5Fe(CO)_2]_2 + SnCl_2{\cdot}2H_2O \xrightarrow[\text{EtOAc}]{CH_3OH} [C_5H_5Fe(CO)_2]_2SnCl_2 \quad [72] \tag{20}$$

No reaction was found to occur[72] with $[C_5H_5Fe(CO)_2]_2$ and $Pb(OAc)_2$ or $PbCl_2$. Likewise, no insertion product was obtained in the reaction[72] of $Mn_2(CO)_{10}$ with $SnCl_2$.

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HETEROGENEOUS CATALYSIS AND SEMICONDUCTING OXIDES

W. Ronald Cares May 10, 1966

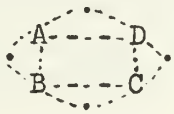
I. Introduction

For many years heterogeneous catalysis and related adsorption phenomena have been the domain of the industrial chemist, working on a hit or miss basis to find some desired catalytic property. Only for the past 15 or 20 years has any major effort been made to try to establish some type of basic relationship between a surface and the catalytic activity it exhibits. It will be the purpose of this seminar to briefly explain, in non-mathematical terms, two current theories of catalysis, the Multiplet and Electronic Theories, to show how modern experimental techniques are used in conjunction with the Electronic Theory, to study surface phenomena, and most important to show that even today with modern experimental techniques workers are still unable to agree on the nature of even a simple system.

II. Physical Adsorption and Chemisorption

The effects of adsorption onto surfaces have been studied since the early 1900's with the work of Langmuir. Adsorption has generally been classified into two types: physical or van der Waals adsorption, characterized by little or no needed energy of activation and small heats of adsorption, and chemisorption, having large energies of activation and large heats of adsorption.[1] The extension of the idea of mono-molecular layer physical adsorption lead to the BET method for the determination of surface areas.[2] The current trend in adsorption studies is to place an important emphasis on the entropy of adsorption along with the heat of adsorption.[3] The entropy of adsorption is of special importance to catalysis as it determines the mobility of the surface species, its ability to migrate to an "active site" for reaction. The importance of surface migration was clearly demonstrated by Weisz who physically mixed two relatively inactive catalysts for the n-hexane isomerization reaction and obtained a relatively active catalyst.[4] Entropy of adsorption considerations also allow endothermic adsorption, limited to very small surface coverages, which becomes important if the adsorbed species is rate determining.

III. Multiplet Theory of Catalysis

The Multiplet Theory of catalysis deals mainly with the geometrical interaction and more recently with the energetics of interaction of a molecule with the surface atoms of a crystal lattice. The application of Multiplet Theory has been mainly in the field of organic catalysis. Balandin, who developed the theory, has recently reviewed it.[5] Multiplet Theory assumes that only certain atoms of a molecule, the indicial group, need interact with the surface of the catalyst. Such an interaction leads to the formation of an activated complex or multiplet similar to that of the absolute reaction rate theory.[6] For two atoms per molecule reacting on a surface we may visualize the multiplet M for the reaction AB + CD $\rightarrow$ AD + BC (a duplet reaction, one that has two bonds broken) as 

where the dots represent surface

atoms. The principle of structural conformity states that the best catalyst for a reaction will be the one that has lattice dimensions such that the atoms of the indicial group fit into the depressions between atoms of the lattice. Thus catalysts should be selective toward certain indicial groups. Substituents on the atoms of the indicial group should be directed away from the catalyst surface and thus stereospecific reactions become possible. Other multiplet reactions are the triplet (1,4-addition to dienes) and the sextet (dehydrogenation of cyclohexane to benzene).

IV. Electronic Theory of Catalysis

The Electronic Theory of catalysis[7] attempts to relate the electrical properties of the adsorbate with those of the solid. Accurate potential energy diagrams for adsorbate and surface may give a qualitative picture of heats of adsorption and energies of activation. As any real bond between an adsorbate and a surface is a mixture of van der Waals, coulombic, and exchange forces, theoretical attempts to estimate adsorbate-surface interactions are generally complicated and result in poor agreement with observed data. Boundary Layer Theory represents a branch of the Electronic Theory which is especially applicable to semiconductors, however an understanding of the band theory of solids is necessary for its discussion.

A. Band Theory of Solids

The development of the electron band theory[8,9] for solids resembles the molecular orbital approach for molecules. We consider first the simple example of a metal, such as sodium. As metal atoms are added to the crystal the allowed electron energies become diffuse about the atomic electron energies. The degree of diffuseness is a function of the internuclear distance in the crystal. For metals the diffuse band of the valence electron level(s) overlaps with the bands from the higher unfilled levels thus forming a "continum" of allowed energies for the valence electrons while the inner electrons remain localized on their respective nuclei. The valence electrons are thus free to "migrate" throughout the crystal lattice allowing metallic conduction. For Group IV A elements the picture is different. Considering N atoms, as the internuclear distance decreases toward its equilibrium value the s-electron band containing 2N allowed electron states first unites with the p-electron band containing 6N states, mixing occurs, and then at smaller internuclear distances approaching the equilibrium distance the 8N mixed states split into two bands of 4N states each. The 4N valence electrons exactly fill the lower band. For conduction to occur the electrons must now jump the forbidden energy region, the band gap, between the lower filled band and the upper empty band. The size of this energy gap will determine if the element will be an insulator or semiconductor. Doping of a semiconductor introduces discrete energy levels into the band gap. If these discrete energy levels contain electrons they may donate these to the upper or conduction band creating an n-type semiconductor; if these levels contain no electrons they may accept electrons from the lower or valence band creating a p-type semiconductor. For mathematical purposes it is necessary to define a Fermi Energy for a semiconductor (the energy level that has a probability of 1/2 of being occupied at temperature T). Its determination is slightly complex[9a,c] and for our purposes we may consider it as lying between the center of the band gap and the impurity levels.

The band schemes for the semiconducting oxides are in general unknown[10] and those presented here are only tentative. For ZnO the valence band arises

from the filled oxide ion 2p orbitals and the conduction band from empty Zn^{2+} ion 4s orbitals; n-type semi conductivity arises from interstitial Zn atoms (see Figure 1a).[11] The band structure for NiO is more complicated. It is thought that the 3d electrons are localized on the nickel ions and that conduction is by holes produced in the oxide 2p valence band by promotion of electrons to nickel $3d^7$ acceptor levels present in the crystal due to a non-stoichiometric excess of oxide ions (see Figure 1b).

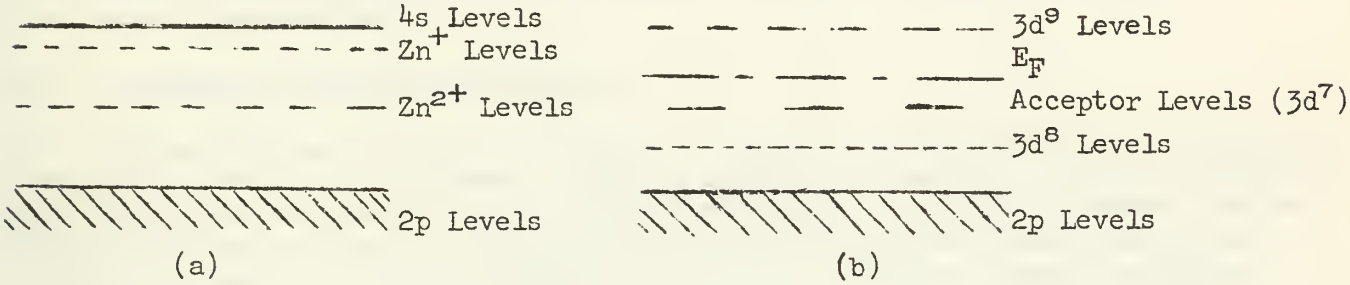


Figure 1.

B. Boundary Layer Theory

Boundary Layer Theory[12] is characterized by the assumption that a gas adsorbed onto a semiconductor acts only as a donor or acceptor of electrons. For mathematical purposes such interactions may be viewed by the theory for metal-semiconductor contacts. A potential energy barrier is established at the surface equal to the difference of the Fermi energies (free energies) of the semiconductor and adsorbate. The theory is capable of precise analysis and correctly predicts that adsorption that removes the major carrier from the semiconductor will be severely limited. The theory also predicts the decrease in the heat of adsorption with increasing coverage without the necessity of postulating a heterogeneous surface or interaction between adsorbed species. The theory predicts rates of adsorption and desorption of the form $A \exp(-eE/kT)$ where both A and E are functions of the surface coverage.[12a] A major objection to the theory is that it does not consider variations in the type of band to the surface. Polarization effects have been considered qualitatively by Weisz.[12a]

V. Electrical Properties of Importance to Catalytic Studies.

The three main electrical properties of semiconductors used in the study of catalysis are the conductivity, the work function and the Hall effect. The conductivity of a semiconductor (σ) is determined by the product of the numbers of conduction electrons, n, or holes, p, and their respective mobilities, μ: $\sigma = e(\mu_n n + \mu_p p)$, where e is the charge of an electron. For a doped semiconductor either n or p will be negligible. The conductivity may also be shown to be the sum of a bulk conductivity (essentially constant) and a surface conductivity. The removal or insertion of electrons at the surface will alter the observed conductivity of the sample. Resistances at grain boundaries are throught to be predominant for polycrystalline samples and the adsorption of an insulating gas layer at these boundaries, if they intersect the surface, may cause meaningless results. The work function is that energy required to remove an electron from the bulk of the solid to infinity and will thus be dependent upon the surface potential created by surface species.[12f] The change

of the work function will thus be related to the change of adsorbed surface species. The Hall effect[8c,13] describes the transverse voltage produced when a magnetic field is applied perpendicular to the current flow in a sample. The Hall coefficient is the reciprocal of the number of conduction electrons (or holes) times the electron charge and is negative for electron conduction and positive for hole conduction. The change in Hall coefficient reflects the number and charge of the adsorbed species. One advantage of the Hall effect is that it is not (or only very slightly) sensitive to grain boundaries, however the experimental techniques are much more difficult to apply than those for conductivity measurements.

VI. Discussion of Experimental Work

During the past 15 years the number of studies on adsorption and catalytic properties have been tremendous. Since a number of excellent reviews[7,11,12b,f,14] are available, no attempt will be made to elaborate on specific systems. Generally, work has centered around an attempt to relate the electronic properties of the catalysts to their activity for a specific reaction; oxygen, hydrogen, and carbon monoxide adsorption and carbon monoxide oxidation have been the systems most studied. The effects of catalyst doping have been studied in most cases. One common observation in the catalysis field is that results of the various studies do not always agree.

A possible reason for this lack of agreement is the wide range of temperatures and pressures investigated—from approximately -100°C to +1000°C and 10^{-3} mm Hg to several atmospheres. Over such magnitudes of temperature and pressure it is not unlikely that the mechanism of adsorption and/or reaction might change. Another possible reason may be the change of surface area of the catalyst with use. Generally the surface area of a catalyst is measured either before or after prolonged use, however recently it has been shown that the surface area may increase by twice to almost 100 times its original area with use.[15] In an attempt to illustrate the principles described above, several selected investigations on the oxidation of carbon monoxide and related adsorption phenomena over NiO and ZnO will be discussed. Table I summarizes the experimental observations of the individual investigators.

A. Nickel Oxide

Parravano studied[16] the carbon monoxide oxidation reaction over pure and silver doped nickel oxide by kinetic methods. An initial high activity region and a constant, temperature dependent activity region were found. The silver doping appreciably decreased the rate of oxidation only in the higher temperature, constant activity region. This effect would be expected if CO^+ entered into the rate determining step of the oxidation reaction. Oxygen pretreatment of the oxides had no effect on the rates of oxidation while carbon monoxide pretreatment eliminated the initial, high activity region. Parravano concluded that the rate of oxidation of carbon monoxide depended upon an adsorbed CO species and upon some type of an adsorbed oxygen species.

Gray and Darby[17] found by using conductivity methods that oxygen adsorption rates were sensitive to the nickel oxide crystal structure. Oxygen was found to adsorb as $O^-_{(ADS)}$ ions and carbon monoxide as a neutral molecule below 200°C and as $CO^+_{(ADS)}$ ions above 200°C. The rate of carbon monoxide oxidation was observed to be controlled by the rate of formation of $O^-_{(ADS)}$ ions. A two zone system—a surface zone and a bulk zone—was proposed to explain different rates of oxygen adsorption.

TABLE I. Summary of Experimental Observations

Investigators(s) (System)	Ref.	Method of Investigation	Approx. Temp. of Investigation, °C	Approx. Pressure of Investigation, mm Hg	Adsorbed CO Species Observed	Adsorbed O Species observed	Effect of CO_2 on Rate of CO Oxidation	CO Oxidation Reaction Dependent upon
Parravano (NiO)	16	Kinetic	180°	280	Yes	Yes	No	$CO_{(ADS)}$ Some ADS. Oxygen Species
Gray and Darby (NiO)	17	Conductivity	250°	0.1	$CO_{(ADS)}$, 200°C $CO^{+}_{(ADS)}$, 200°C	$O^{-}_{(ADS)}$	Yes	$O^{-}_{(ADS)}$
Roberts and Wells (NiO)	18	Work Function	23°	0.05	$CO^{+}_{(ADS)}$	$O_2(ADS)$ $O^{-}_{(ADS)}$	No	$CO^{+}_{(ADS)}$ $O^{-}_{(ADS)}$
Bevan and Anderson (ZnO)	20	Conductivity	500°-1000°	0.01	------	$O_2(ADS)$ $O^{-2}_{(ADS)}$	----	------
Amigues and Teichner (ZnO)	21	Conductivity Kinetic	260	3	$CO_{(ADS)}$	$O_{(ADS)}$ $O^{-}_{(ADS)}$	Yes	$CO_{(ADS)}$ $O_{(ADS)}$
Chon and Prater (ZnO)	22	Hall Effect	350	0.5	$CO_{(ADS)}$	$O^{-}_{(ADS)}$ ($O_{(ADS)}$ and/or $O^{-}_{2(ADS)}$?)	----	$CO_{(g)}$ $O^{-}_{(ADS)}$

Roberts and Wells[18], using work function measurements, observed that oxygen adsorbed on nickel oxide as both $O_2(ADS)$ and $O^-(ADS)$ species. Carbon monoxide adsorbed as a $CO^+(ADS)$ species while carbon dioxide adsorbed as a neutral species. A decrease of catalytic activity was noted for successive carbon monoxide oxidations over the same catalyst sample; carbon dioxide had no effect on the rate of activity decrease. Oxygen adsorption was observed to be more rapid than carbon monoxide adsorption and oxygen adsorption poisioned the catalyst toward the carbon monoxide reaction.

Another study[19] showed that oxygen adsorption is dependent upon the surface concentration of Ni^{3+} ions in nickel and nickel-lithium doped magnesium oxide samples.

B. Zinc Oxide

Bevan and Anderson[20] studied oxygen adsorption on zinc oxide by conductivity methods. Both adsorbed $O_2(ADS)$ molecules and $O^{-2}(ADS)$ ions were observed. A rearrangement of the zinc oxide surface atoms to create a heterogeneous surface was proposed to explain adsorption characteristics at low pressures.

Recently Amigues and Teichner[21] have studied the carbon monoxide oxidation reaction over zinc oxide by simultaneous conductivity and kinetic measurements. Oxygen adsorption was found to be as $O(ADS)$ atoms and $O^-(ADS)$ ions, while both carbon monoxide and carbon dioxide were adsorbed as neutral molecules. A competition for the same type of adsorption site was noted for oxygen, carbon monoxide, and carbon dioxide. A second type of adsorption site was also observed. The oxidation of carbon monoxide was found to depend upon oxygen atoms adsorbed on one type of adsorption site and upon carbon monoxide adsorbed on a different type of adsorption site. Similar studies on Li^+ and Ga^{3+} doped zinc oxide samples confirmed that the adsorbed oxygen atom was the reactive oxygen species.

Chon and Prater[22] studied the carbon monoxide oxidation reaction over indium doped zinc oxide by Hall effect measurements. Oxygen adsorption was accompanied by the loss of one electron from the conduction band for each oxygen atom adsorbed, thus indicating $O^-(ADS)$ species. Carbon monoxide and carbon dioxide were adsorbed as neutral species. The oxidation of carbon monoxide was accompanied by the donation of one electron to the conduction band for each carbon monoxide molecule oxidized, thus indicating that the $O^-(ADS)$ ion is the reactive oxygen species.

VII. Conclusion

In summary, we have seen that heterogeneous catalysis is a very broad and still relatively unknown field. Two major theories, the Multiplet Theory and the Electronic Theory, of catalysis have been briefly described. The application of the Electronic Theory to the semiconducting oxides nickel oxide and zinc oxide has been discussed. Through specific examples the application of conductivity, work function, and Hall effect measurements to the problem of elucidation the nature of gas-surface interactions has been examined.

It is important to point out that the ideas discussed need not be applied solely to the interaction of oxygen and carbon monoxide with a solid oxide phase but in general may be applied to any gas or liquid phase in contact with its container. The most important point, however, to emphasize is that the field is not cut and dry, that the techniques are not well established, and that results of studies are not unambiguous. This last point is best pointed out by the last two papers discussed where two men, both well established in the catalysis field, can study essentially the same system at essentially the same experimental conditions and arrive at opposite conclusions as to the nature of an adsorbed oxygen species.

The field of catalysis is always open for new and interesting basic research. With the techniques of nmr , esr , NQR , and low energy electron diffraction now fairly well established and just now beginning to be mentioned in connection with heterogeneous catalysis studies it is probable that the next few years should yield considerable advances in our knowledge of surface phenomena.

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NUCLEAR MAGNETIC RESONANCE STUDIES OF ORGANOMETALLIC EXCHANGE REACTIONS

Larry M. Seitz May 17, 1966

Introduction

In order to fully understand the mechanisms of reactions of organolithium compounds in donor solvents, more information concerning their behavior in these solvents is needed. Nuclear magnetic resonance is a particularly useful tool since it has the capability of measuring rates of rapid reactions, and both proton and ^7Li resonances can be easily obtained. Therefore it is possible to obtain exchange rate and activation energy parameters for both lithium and alkyl group exchange, information which is of great value in deciding on a mechanism for the process.

Various aspects of organolithium compounds are discussed in a recent review[1]. Evidence for mixed associated species has been obtained by lithium-7 spectra of mixtures of organolithium compounds in hydrocarbon solvents[2,3]. This technique has been extended to obtain the association of methyl- and ethyllithium in ether[4]. Inversion at the metal-bearing carbon of neohexyllithium in ether was recently investigated[5]. In general, exchange reactions proceed more rapidly in donor solvents, e.g. ether, than in hydrocarbon solvents. Ether was the only solvent used for the systems discussed in this seminar.

Organolithium Exchanges

In order to gain some knowledge of the association of methyl- and ethyllithium in ether, mixtures of these compounds were investigated. Lithium-7 data at -80°C provide evidence of association with the appearance of four resonances sensitive to the methyl/ethyl ratio. The spectra are accounted for by assuming a random distribution of the two alkyl groups in groups of three, e.g. the four possibilities: 3Me; 2Me and 1Et; 1Me and 2Et; 3Et. Although the data could be interpreted in terms of trimeric association with rapid intramolecular exchange, it is more attractively accommodated to a tetramer model assuming slow intramolecular exchange. The structure of the tetramer is considered to be that postulated earlier for solution and gaseous species[6], and observed in the crystal structures of methyl-[7], and ethyllithium[8]. The observed spectra can then be explained by a "local environment" hypothesis; the chemical shift of a lithium in a mixed species is determined by the three neighboring alkyl groups only[3,4]. The reported three-fold association of methyllithium in boiling ether[9] can be ascribed to some dissociation of the form $R_4Li_4 \longrightarrow 2R_2Li_2$.

The temperature dependence of the ^7Li and proton linewidths of methyllithium give evidence for lithium-proton coupling and show that the slow exchange region is reached at about -50°C. Lithium-7 data for ethyllithium suggest exchange is faster. The exchange process is most likely of the form $Li_4R_4 \rightleftarrows 2Li_2R_2$. Inversion[5], presumably through the intermediacy of a carbanion $R_4Li_4 \rightleftarrows R_3Li_4^+ + R^-$, appears to be slower than alkyl group exchange in methyl- and ethyllithium.

Methyl-, phenyllithium and ethyl-, phenyllithium mixtures have also been examined at low temperature by proton and lithium-7 spectra, respectively. The data can be interpreted in terms of phenyllithium being dimeric, in agreement with ebulliometric measurements[9,10], and further support four-fold association for methyl- and ethyllithium.

CH_3Li-$(CH_3)_2Mg$ and CH_3Li-$(CH_3)_2Zn$ Systems

Proton and ^7Li spectra of ether solutions of methyllithium with dimethylmagnesium and dimethylzinc have been examined over a large temperature range. The spectra show that complex species of the form $Li_2M(CH_3)_4$ and $Li_3M(CH_3)_5$ (M = Mg, Zn) are formed. It is proposed that the latter species, which forms when the ratio Li/M>2, results from the replacement of one lithium atom in the tetramer structure by a magnesium or zinc atom. In contrast to the phenyl complexes isolated by Wittig et al.[9], no 1:1 complex was observed. However, the complex $Li_2Zn(CH_3)_4 \cdot O(C_2H_5)_2$ has been reported[11].

Exchange of lithium between methyllithium and complex appears to occur at about the same rate, and with the same activation energy, as methyl group exchange. The exchange processes are faster in the zinc than in the magnesium system. It appears that in the zinc system the rate-determining process is dissociation of methyllithium tetramer to dimers. Methyl group exchange between $(CH_3)_2M$ and $Li_2M(CH_3)_4$ is also faster in the zinc than the magnesium system, even rapid at -107°C in the zinc system.

Exchange of methyllithium with $LiB(CH_3)_4$ and $LiAl(CH_3)_4$ has been studied in detail by Williams and Brown[12]. Lithium-7 exchange was found to obey the same kinetics in the two cases and evidence is given for dissociation of methyllithium tetramer as a rate-determining step: $(Li_4CH_3)_4 \rightleftharpoons 2(LiCH_3)_2$. This was helpful information in the interpretation of the zinc and magnesium systems.

C_6H_5Li-$(C_6H_5)_2Mg$ and C_6H_5Li-$(C_6H_5)_2Zn$ Systems

Lithium-7 spectra illustrate that the complex $Li_2M(C_6H_5)_4$ is formed in solution when the Li/M ratio ≥ 2, but unlike the methyl system, no $Li_3M(C_6H_5)_5$ species is observed. Some formation of a 1:1 complex, $LiM(C_6H_5)_3$, when Li/M $\not< 2$ cannot be ruled out.

Lithium exchange between phenyllithium and $Li_2M(C_6H_5)_4$ has been examined from room temperature to -58°C. The exchange parameters for the zinc and magnesium systems are very similar.

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